

Utilization of Low Nox Coal Combustion By-Products

**Quarterly Report
July 1 - September 30, 1996**

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DE-FC21-94MC31174**

**PROJECT SUMMARY - EIGHTH QUARTER
July 1, 1996 through September 30, 1996**

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TECHNOLOGY TRANSFER

Michigan Technological University has signed an agreement with Mineral Resource Technology, LLC (MRT) of Atlanta, Georgia to commercialize the fly ash beneficiation technology. This agreement was finalized July 1, 1996. MRT intends to commercialize the technology through development and operation of various facilities around the country.

The commercialization process began with press releases to various trade publications. Copies of these releases are given in Appendix A. The next step was to invite interested parties to attend a demonstration of the technology. This was held on September 26, 1996 at IMP/MTU. A copy of the invitation is given in Appendix B. Six representatives from a variety of utilities and other associated industries attended and at least twice as many more companies expressed interest but were unable to attend that session. It is too early to say how commercialization will proceed at this point but initial response to the technology is favorable and several companies are very interested.

TASK 1.0 - TEST PLAN

This task has been completed.

TASK 2.0 - LABORATORY CHARACTERIZATION

Task 2.1 - Sample Collection

No new samples were received this quarter. We do not expect to collect any additional samples for this project.

Task 2.2 - Material Characterization

To determine if there was any difference in the elemental composition of different sizes of the fly ash, elemental analysis of each individual size fraction (+65 mesh, +100, +150, +200, +270, +325, +400, and -400 mesh) for the five as-received and clean ash samples were conducted. The five ash samples are AEP, BGE, NPC, CPC, and DE2. All the samples were scanned using a Leeman Labs PS950 Inductively Coupled Plasma Spectrometer (ICP). The ICP was calibrated to quantitatively determine the concentrations of seventy elements. Trace elements that were present in measurable quantities included Cu, Zn, Ce, Sr, B, Y, Ba, Co, Be, and As. Graphs showing the raw data are included in Appendix C.

Water analyses of the filtrate from the clean ash and carbon concentrate streams were

obtained. These were grab samples taken during pilot plant runs of NPC (Class C) ash, AEP (Class F) ash, and DE2 (mixture) ash. A sample of fresh water coming into the plant was also analyzed for comparison. The process water analyses were compared to Drinking Water Standards Maximum Contamination Levels. The preliminary analytical results for each of the three ash samples are also given in Appendix C.

Task 2.3 - Laboratory Testing of Ash Processing Operations

Screening Tests

Tests were conducted to establish the parameters for dry screening the ash prior to introduction into the wet beneficiation phase of the process. Initial results indicate that if an ultrasonic unit is attached to the screen, considerably greater throughput can be realized, at the same time, plugging of the screen can be nearly eliminated. Samples of as-received ash were sent to Russell-Finex and SWECO for testing.

Russell-Finex has completed the requested tests at 325 mesh, with positive results, however the capacity was low. Since it is likely that, if used at all, the screening operation would employ a 100 mesh screen, the throughput would increase dramatically. This appears to be an ash specific unit operation.

The tests at SWECO have also been completed. These tests indicated that, at the anticipated throughput of a commercial operation, the operating cost was much higher than could be tolerated. These systems work well on a small scale but the machine displayed excessive wear after being subjected to the highly abrasive clean ash fraction (alumina and silica) for extended periods of time.

Centrifuge Tests

Centrifuge tests have indicated that the use of a centrifuge is a realistic option. The resulting products are good quality and low moisture. Two commercial case studies using centrifuge systems to process ash were obtained. These indicate that the ash can be dewatered using the centrifuge without resulting in excessive wear along the surface of the bowl or scroll components of the centrifuge. Use of centrifuges will result in lower capital and lower operating costs, while also producing a material with lower moisture when compared to using a vacuum filter dewatering system. This in turn results in reduced thermal drying costs.

Drying systems, such as the Denver Holoflite dryer, were evaluated. The company has tested drying ash products with successful results

TASK 3.0 - PILOT PLANT TESTING

The pilot plant was run for the demonstration held on September 26. The utility industry representatives were given individual tours of the circuit to familiarize them with how the separation occurs, what types of equipment are used, and what the resulting products are like. In addition, fly ash was used to demonstrate froth flotation to a delegation from Chrysler/Vehicle Recycling Partnership (VRP) and the American Plastics Council (APC). That group is funding plastics separation using froth flotation at IMP and was interested in how the technology worked.

In May and June, the Metallurgical and Materials Engineering Department conducted a Mechanics of Mill Practice class which incorporated fly ash beneficiation. The students conducted laboratory and pilot plant tests using a fly ash from Detroit Edison. A copy of the report will be included when it is available.

TASK 4.0 - PRODUCT TESTING

Activities are underway in all five subtasks.

Task 4.1 - Concrete Testing

A detailed analysis has been completed for utilizing Class C Nevada Power Company (NPC) fly ash to replace cement in concrete manufacturing. This analysis included characterization of as-received and cleaned ash, testing the performance of ash-cement-water mixtures, and determining the mechanical properties of the concrete.

Characterization of As-received and Cleaned NPC Ash

Table 1 details the chemical composition of as-received and cleaned NPC ash. From Table 1, SiO_2 increased from 56.9% before processing to 59.2% after processing. CaO decreased from 11.2% to 8.9% after separation. The percentage of Al_2O_3 and LOI slightly decreased from 16.3% and 4.6% to 16% and 4.2%, respectively.

Size analyses were obtained with Tyler sieves for the fractions larger than 400 mesh (37 microns) and Microtrac Analyzer for the -400 mesh fraction. The results are recorded in Tables 2 and 3, respectively. From Table 2, the percentage of cleaned ash passing +150 mesh significantly increased after separation. However, the amount of fine particles in cleaned ash passing 400 mesh decreased after separation. A portion of the fine and soluble particles are lost during the beneficiation process. The fly ash particles passing 400 mesh were further analyzed with the Microtrac Analyzer, and the results (Table 3) indicate that there was no significant size change between the cleaned ash and the as-received ash.

Table 1
Chemical composition of as-received and cleaned NPC ash

Chemical Composition	As-received fly ash (%)	Cleaned fly ash (%)	ASTM C 618 (Class F ash)
Al ₂ O ₃	16.31	15.99	
SiO ₂	56.93	59.22	
Fe ₂ O ₃	4.3	3.71	
<i>Total (SiO₂+Al₂O₃+Fe₂O₃)</i>	77.5	78.92	70 (minimum)
CaO	11.18	8.94	
Mg	2.04	2.03	
Na ₂ O	2.84	3.33	
K ₂ O	0.72	0.54	
TiO ₂	0.90	0.76	
P ₂ O ₅	0.17	0.06	
LOI	4.60	4.20	6.0 (maximum)
Total	99.95	98.98	

Table 2
Particle size and distribution of as-received ash and cleaned NPC fly ash

Tyler Mesh	As-received ash			Cleaned ash		
	Weight %	Individual %	Cumulative%	Weight %	Individual %	Cumulative%
+65	2.40	2.30	2.30	0.00	0.00	0.00
+100	1.20	1.15	3.45	0.00	0.75	0.75
+150	2.20	2.11	5.56	0.60	1.12	1.87
+200	4.20	4.02	9.58	3.40	6.34	8.21
+270	5.60	5.36	14.94	6.20	11.57	19.78
+325	4.60	4.41	19.35	7.20	13.43	33.21
+400	6.60	6.32	25.67	4.60	8.58	41.79
-400	77.60	74.33	100.0	31.20	58.21	100.0

Table 3				
Microtrac analysis of particle size distribution for NPC ash passing 400 mesh				
Channel	As-received ash		Cleaned ash	
	Cumulative (%)	Volume (%)	Cumulative (%)	Volume (%)
62	100.0	2.6	100.0	3.2
44	97.4	9.1	96.8	9.7
31	88.3	11.4	87.1	12.2
22	76.9	12.0	74.9	12.1
16	64.9	11.7	62.8	12.2
11	53.3	10.2	50.6	10.6
7.8	43.1	9.6	40.0	9.4
5.5	33.5	7.5	30.5	7.6
3.9	26.0	9.2	22.9	8.4
2.8	16.7	9.6	14.5	8.4
1.9	7.2	4.0	6.1	3.5
1.4	3.2	2.5	2.6	2.1
0.9	0.7	0.7	0.5	0.5

The microscopic structures of as-received and cleaned NPC fly ash were observed by scanning electron microscopy (SEM). Figure 1 shows that the as-received ash mainly consists of round and spherical particles. There are also irregular particles, including unburned coal remnants and mineral particles. Figure 2 shows that the cleaned ash also consists of round and spherical particles, as well as some irregular particles, but there are less fine particles in the cleaned ash than in the as-received ash.

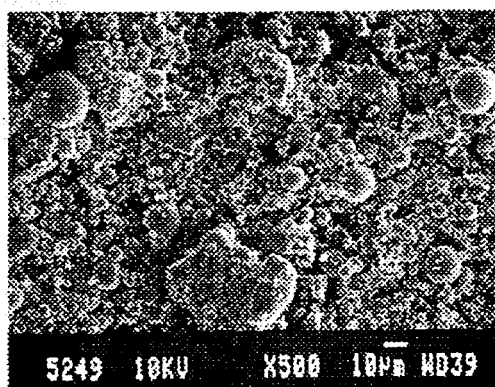


Figure 1. As-received NPC ash

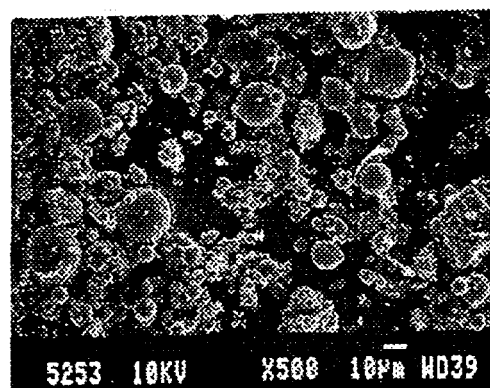


Figure 2. Cleaned NPC ash

Concrete Performance

Table 4 shows the water requirement, workability of fresh fly ash-cement-water mixture, and compressive strength of the concrete. The water to cement ratio was designed at 0.5 for Grade 35S concrete. When both as-received and cleaned ash were separately used to replace cement, the water to cementitious material ratio decreased with the amount of cement replaced by the ash in order to obtain the desired slump value. Low water requirement of both as-received and cleaned ash-cement-water mixtures is mainly due to the particle morphologies of the NPC ash. A high proportion of fine and smooth spherical particle shapes in the ash acts to improve the rheological properties of fresh concrete paste.

Table 4 Effects of amount of cement replaced by fly ash and curing period on concrete properties

Concrete grade and type		W/C ^a ratio	Slump in	Air %	Density pcf ^b	Compressive strength (psi)		
						7 day	28 day	91 day
Grade 35S concrete with as-received ash	0%	0.50	3.50	7.1	148.8	3692	4676	5512
	8%	0.49	3.50	1.5	152.8	4393	6260	7304
	20%	0.49	4.00	2.0	151.8	4187	5992	7738
	30%	0.47	3.50	2.0	151.6	3657	5271	7326
	40%	0.44	3.25	2.0	150.9	3257	5277	7467
	50%	0.43	3.75	1.59	151.4	2344	4121	6302
	60%	0.43	4.00	1.69	151.2	1507	2980	5118
Grade 35S concrete with cleaned ash	0%	0.50	3.50	7.1	148.8	3692	4676	5512
	8%	0.48	3.50	5.0	147.6	3557	4488	5833
	20%	0.47	3.75	4.0	149.0	3404	4929	6160
	30%	0.45	3.00	3.0	150.8	3298	4423	5624
	40%	0.45	3.25	3.75	147.1	2774	4399	5736
	50%	0.45	2.00	3.0	143.4	2044	3651	4735
	60%	0.44	2.25	3.5	146.4	1519	2684	4105
Grade 30S concrete with cleaned ash	0%	0.52	2.50	7.0	146.4	3474	4158	4399
	20%	0.50	2.50	4.8	149.2	3021	4323	4977
	30%	0.49	3.50	2.8	148.7	2650	4205	5045
Grade 40S concrete with cleaned ash	0%	0.49	4.0	5.5	148.4	3981	4823	5412
	20%	0.43	2.75	5.25	148.6	3864	5118	5683
	30%	0.43	4.0	3.9	149.0	3339	5029	6125

Note: a) W/C (water to cementitious materials) ratio is the ratio of water/(cement + fly ash).

b) pcf is pound per cubic yard.

The air content in fresh cement paste without fly ash was 7.1%. When the as-received ash was added, the air content was reduced to 2% or less. When the carbon content was reduced by the beneficiation process, the air content in the cleaned ash-cement-water mixture had an average 3.7% for grade 35S concrete, an average 3.8 % for grade 30S concrete, and an average 4.57% for grade 40S concrete. All fresh concrete mixtures entrap a certain amount of air during mixing. It is important for there to be air in concrete to improve the workability of the fresh cement mixture, increase the impact strength of concrete, and improve the freeze/thaw behavior of the concrete. When as-received ash was added into the mixture, carbon particles in the ash adsorb the air entraining agent in fresh concrete because of their high specific surface area and sorption capacity, which decreases the air content in the concrete. In order to keep a equal level of air in the ash-cement-water mixture as the concrete without ash, air entraining agent has to be added at a much higher dosage than usual. When the carbon content is reduced by the beneficiation process, the air content in the cleaned ash-cement-water mixture is significantly increased in all three grades concrete in comparison to the fresh concrete with as-received fly ash.

Mechanical Properties of the Concrete

Figure 3 shows the effects of the amount of cement replaced by fly ash and the curing period on the compressive strength of Grade 35S concrete. The concrete with 8% and 20% as-received ash had higher seven day compressive strengths than the concrete without fly ash. Other concrete with as-received ash had low seven day compressive strength in comparison to the concrete without fly ash. All the concrete with cleaned ash had lower seven day compressive strength than the concrete without fly ash. The concrete with 8, 20, 30, and 40% as-received ash and 20% cleaned ash had high 28 day compressive strength in comparison to the concrete without fly ash. The 28 day compressive strengths of both as-received and cleaned ash concrete, except for the sample replacing 60% of the cement, were over 3500 psi, which satisfies the design requirements. The 91 day compressive strength of the concrete with 8, 20, 30, and 40% as-received fly ash were over 7000 psi, double the design strength (3500 psi). All concrete with as-received fly ash had higher 91 day compressive strength than the concrete without fly ash, except the concrete with 60% as-received fly ash. All the concrete with cleaned ash had high 91 day compressive strength in comparison to the concrete without fly ash except the concrete with 50 and 60% cleaned fly ash.

Compared to the concrete without fly ash, the concrete with fly ash has a low early strength, except the concrete with 8% and 20% as-received ash. The concrete with fly ash has a fast strength development from 28 to 91 days, so that the concrete of both as-received and cleaned ash have higher 91 day compressive strengths than the concrete without fly ash when up to 40% of the cement is replaced by fly ash. The low early strength of concrete with fly ash is due to less heat generated from the hydration reaction of cement when cement is partially replaced by fly ash. The high strength of concrete with fly ash after the 91 day curing period results from the low water content and high calcium content in fly ash which have cementitious as well as pozzolanic properties.

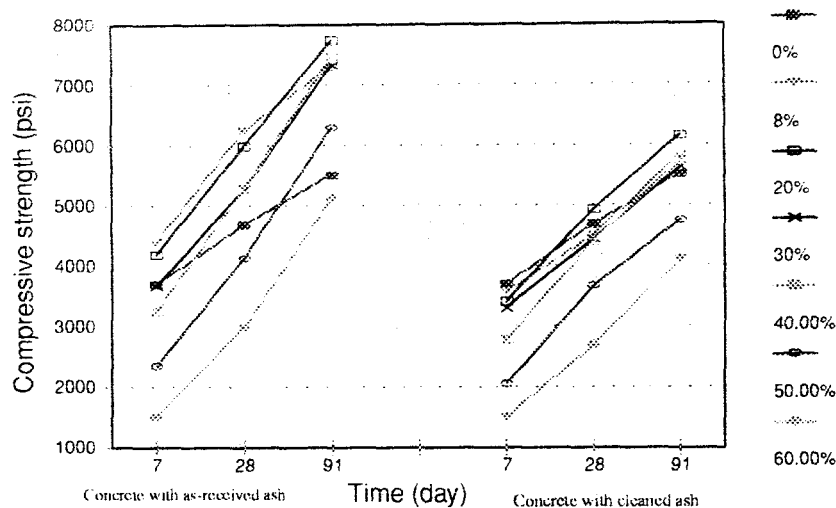


Figure 3 Effects of amount of cement replaced by fly ash and curing period on compressive strength of concrete

The concrete with cleaned ash has relatively low compressive strength for all ash levels and curing periods in comparison to the concrete with as-received ash. The reason for this is not clear. A possible reason is the loss of fine particles and soluble components, such as CaO, during the beneficiation process, which may influence the pozzolanic properties of the cleaned ash. Further studies are needed to verify this.

Figure 4 shows compressive strength of grades 30S, 35S and 40S concrete with and without cleaned NPC ash. All the grades of concrete with cleaned ash had lower seven day compressive strength than the same grades of concrete without fly ash. All the 28 day compressive strengths of concrete with cleaned ash were higher than the strength of the concrete without fly ash, except the grade 35S concrete with 30% cleaned ash. For all three grades, the 28 day compressive strength of concrete with and without cleaned ash met the design requirements. The concrete with cleaned ash had a fast strength development from 28 to 91 days for all three grades in comparison to the concrete without fly ash. The 91 day compressive strength of grade 30S concrete including 20% and 30% cleaned ash were, respectively, 4977 and 5045 psi, which is higher than the strength of concrete without fly ash (4399 psi). The 91 day compressive strength of grade 35S concrete including 20% and 30% cleaned ash were, respectively, 6160 and 5624 psi which is much higher than the strength of concrete without fly ash (5512 psi). The 91 day compressive strength of grade 40S concrete including 20% and 30% cleaned ash were, respectively, 5683 and 6125 psi which is higher than the strength of concrete without fly ash (5412 psi).

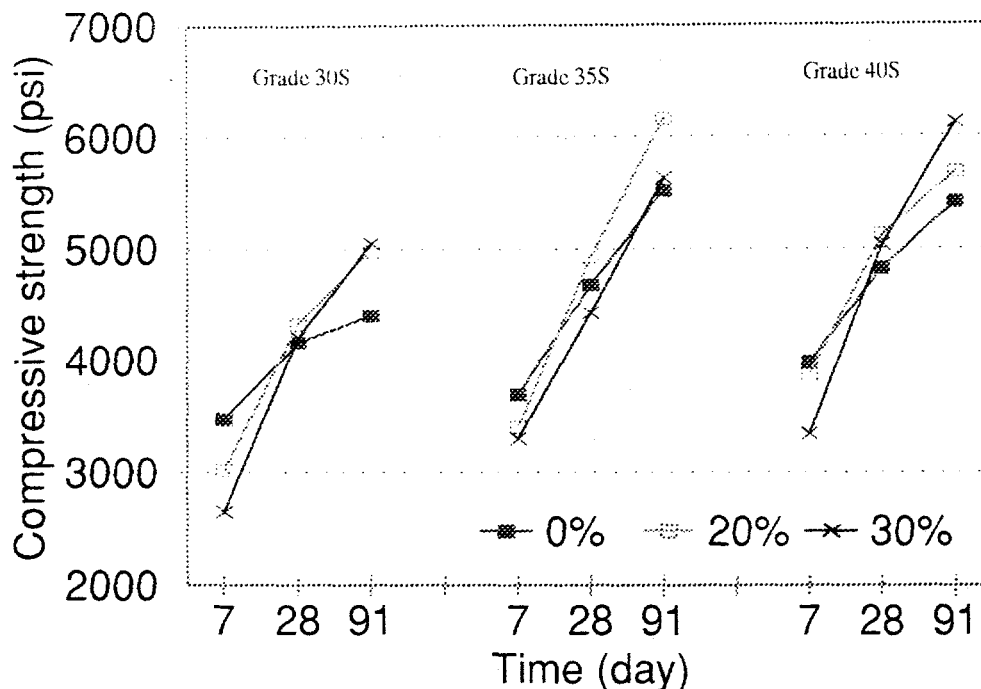


Figure 4 Effects of amount of cement replaced by cleaned fly ash, curing period, and concrete grade on compressive strength of concrete

Concrete Conclusions

Several conclusions can be drawn from the study:

1. A Class C ash was collected from low NO_x burner of Nevada Power Company (NPC) with an average LOI value of 4.6%. The beneficiation process was employed to separate carbon, cenospheres, and magnetic materials from the as-received ash, which reduced the carbon content and LOI value.
2. After separation using the beneficiation process, other changes of chemical composition include: SiO₂ increased from 56.93% to 59.22%. CaO decreased from 11.18% to 8.94% after separation. Al₂O₃ and LOI slight decreased from 16.31% and 4.6% to 15.99% and 4.2%, respectively.
3. From the analysis of fly ash size and microstructure, the cleaned ash passing +150 mesh significantly increased after separation. However, fine particles in cleaned ash passing 400 mesh decreased after separation. Scanning electron micrographs proved that both as-

received and cleaned ash were composed of spherical particles and irregular particles. The fine particles in cleaned ash are less than that in as-received ash.

4. In fresh concrete paste, the water to cementitious material ratio decreased with the amount of cement replaced by both as-received and cleaned ash in order to obtain the desired slump value. Air content in the mixture greatly decreased as the as-received ash was added. The air content in the mixture also dropped as the cleaned fly ash was added. However, the air in the concrete with cleaned ash is much higher than the air in the concrete with as-received ash.
5. The concrete with the fly ash had a lower early strength than the concrete without fly ash except the concrete specimens with 8% and 20% as-received fly ash. The concrete with the fly ash has fast strength development during the 28 to 91 day curing period. All the concrete with cleaned ash had high 91 day compressive strengths when cement was replaced by fly ash up to 40% in comparison to the concrete without fly ash in grade 35S concrete. The concrete formed with either as-received or cleaned fly ash replacing up to 50% of the cement for a 35S design strength mixture meets compressive strength specifications.

A paper entitled "Utilization of Beneficiated Low NO_x Fly Ash in Concrete and Concrete Block" has been submitted for presentation at the American Coal Ash Association's (ACAA) Twelfth International Symposium on Management and Use of Coal Combustion Byproducts. This symposium will be held in Orlando, Florida on January 26-30, 1997. A copy of the paper is included in Appendix D.

Task 4.2 - Concrete Block/Brick

Table 5 shows the density, moisture content, absorption, and compressive strength of concrete blocks made with and without NPC as-received and cleaned fly ash at various curing periods. The moisture content in blocks without fly ash averaged 37.8% for all curing periods, which is higher than the blocks with as-received or cleaned ash. The absorption in blocks without fly ash averaged 7.5% for all curing periods, which is lower than the blocks with as-received or cleaned ash. This is probably related to the cement ratio in the blocks. Higher cement content in the blocks (without ash) requires more water for the hydration reaction, which results in high moisture content. After curing, the cement in the blocks resists absorbing moisture from the atmosphere.

Figure 5 shows the effects of fly ash type, amount of cement replaced by fly ash, and curing period on the compressive strength of concrete blocks. All the concrete samples containing fly ash had lower compressive strengths than the concrete without fly ash throughout

all the curing periods, except the concrete with 15% fly ash at the 28 day curing period. The concrete with 20% cleaned ash had lower one and seven day compressive strengths than the concrete with 20% as-received ash. The concrete with 20% cleaned ash had higher 14 and 28 day compressive strengths than concrete with 20% as-received ash. The compressive strengths decreased with the increase of cleaned ash in blocks throughout all the curing periods. The 28 day compressive strengths of both as-received and cleaned ash concrete met design requirements.

Similar to what occurred with concrete made from NPC ash, the concrete blocks with fly ash had a lower early strength than the concrete without fly ash. The concrete blocks formed with either as-received or cleaned NPC fly ash replacing up to 30% of the cement meets the 28 day compressive strength specifications.

Table 5
Physical and mechanical properties of concrete block

Test period	Block properties	Block without fly ash	Block with 20% as-received ash	Cleaned ash content in block		
				15%	20%	30%
1 day	Density (pcf ^a)	138.2	129.0	133.0	132.3	132.3
	Moisture content (%)	37.8	21.4	23.8	21.5	21.5
	Absorption (pcf)	7.5	9.0	7.9	9.1	9.1
	Compressive strength (psi)	2260	1420	1870	1220	1050
7 day	Density (pcf)	138.2	134.5	133.0	136.0	138.4
	Moisture content (%)	37.8	13.2	26.8	26.0	21.3
	Absorption (pcf)	7.5	8.2	7.9	8.2	9.6
	Compressive strength (psi)	3120	2450	2860	2380	2190
14 day	Density (pcf)	138.2	133.2	133.0	136.0	132.3
	Moisture content (%)	37.8	34.4	23.8	26.0	21.5
	Absorption (pcf)	7.5	8.7	7.9	8.2	9.1
	Compressive strength (psi)	3310	2520	2950	2720	2240
28 day	Density (pcf)	138.2	134.8	133.0	136.0	135.4
	Moisture content (%)	37.8	28.1	26.8	26.0	25.3
	Absorption (pcf)	7.5	8.2	7.9	8.2	7.2
	Compressive strength (psi)	3290	2420	3320	2830	2350

^a pcf is pounds per cubic yard.

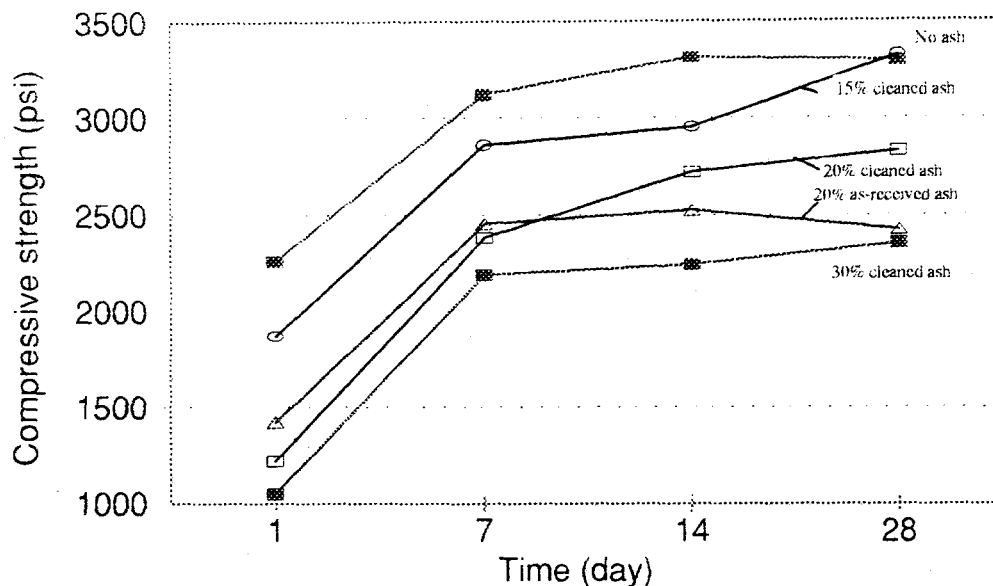


Figure 5 Compressive strength of concrete block

Task 4.3 - Plastic Fillers

The experimental work in this task is complete. Analysis of the test data is nearly finalized and the results are very promising.

A paper entitled "Processed Low NO_x Fly Ash as a Filler in Plastics" has been submitted for presentation at the American Coal Ash Association's (ACAA) Twelfth International Symposium on Management and Use of Coal Combustion Byproducts. This symposium will be held in Orlando, Florida on January 26-30, 1997. A copy of the paper is included in Appendix E.

Task 4.4 - Activated Carbon

Further data analysis, examining the effect of temperature and time on activation of NPC fly ash carbon, using CO₂ as an activation agent was conducted during this quarter. The BET surface area and LOI after activation at different temperatures and time are presented in Figure 6 and Figure , respectively.

It appears that higher temperature and longer time favors activation at the current experimental conditions, which were a fixed flow rate of both CO₂ and argon of 1.8 liters per minute. At 600°C and 700°C, the surface area and LOI remained essentially unchanged no matter the how long the activation lasted. A slight increase in the BET surface area and decrease in LOI was observed at 850°C. At 900°C for a activation time of 120 minutes, the BET surface

area was increased from 44 to 65 m²/g, with a decrease of LOI from 70% to 42%. Further tests are in progress to optimize the activation conditions. Also the adsorptive properties of the activated carbon are under determination.

The following will be tested in the next period:

- Optimizing activation conditions, including CO₂ flow rate, activation temperature and time, and load of carbon.
- Conducting adsorption isotherms of molasses as well as BET surface area to overall evaluate the activation.

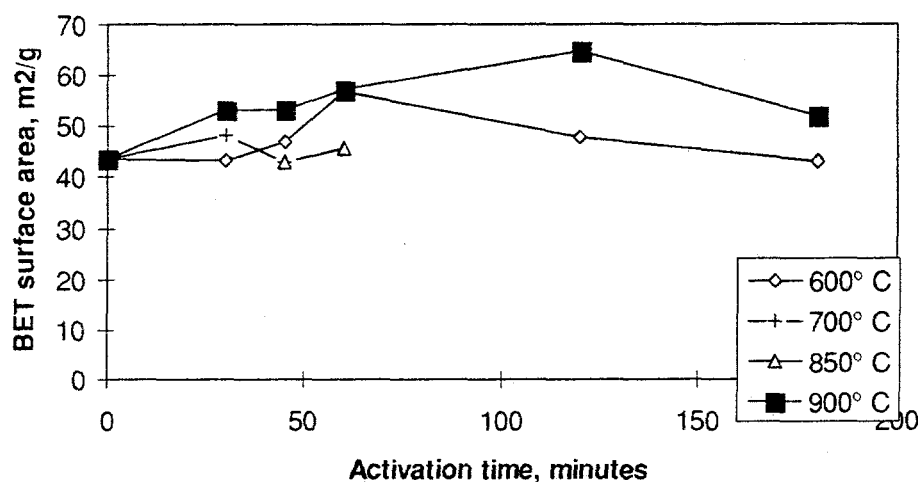


Figure 6. BET surface area as a function of activation time

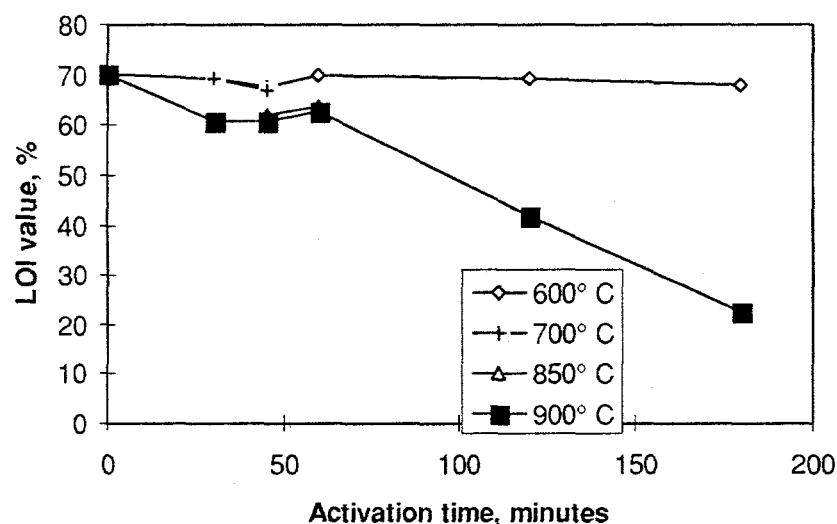


Figure 7. LOI value as a function of activation time

Task 4.5 - Metal Matrix Composites

In order to estimate the potential mechanical properties of aluminum / fly ash composite a new fabrication route was explored. A flow diagram of this process is shown in Figure 8.

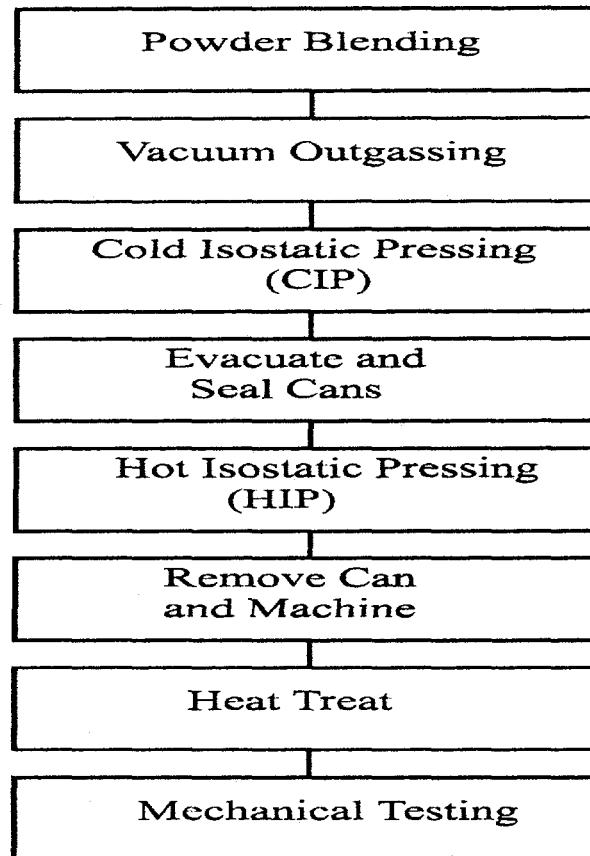


Figure 8. Aluminum / Fly Ash Composite Fabrication Process

The processing route includes; blending elemental powder and appropriate amount of fly ash, vacuum out gassing the composite powder, and cold isostatically pressing (CIP) 5/8" diameter rods. The compacted green rods are then wrapped in graphoil (a sheet of carbonaceous material approximately 0.010" thick) and placed in a 3/4" copper tubing. The graphoil is necessary as a protective barrier to prohibit incipient melting between the copper canning material and the aluminum compact. The copper tubing is then vacuum out gassed and sealed by TIG welding. The cans are hot isostatically pressed (HIP) under an argon atmosphere. The bars are machined into round tensile bars per ASTM standard E8. The bars are then heat treated at 513°C

for 1 hour, cold water quenched, and held at 170°C for 18 hours. Heat treated round tensile specimens are tested per ASTM standard E8.

During this quarter, tensile bars were made with 0, 10, and 20 v/o loading of fly ash. The matrix material was 2124 elementally blended powder. Tensile bars, HIP'ped at two different temperatures, were produced. The first HIP temperature used was 500°C. After heat treating, the microstructure of this material was examined. Large particles of copper were apparent in the microstructure. The particles were 35-60 μm in size, close to the size of the original powder particle. A microphotograph of the microstructure is shown in Figure 9. With elemental powder it was apparent that there was no liquid present during HIP'ping. The solidus temperature of Al-Cu is 548°C. Therefore, it was decided to use 560°C as the second HIP temperature. Again after heat treating the microstructure was examined and the copper was found to be dispersed into the matrix with some sub micron size copper particles are still visible. This microstructure is shown in Figure 10. The microstructure is taken on an SEM using backscattered electron imaging (BEI). BEI highlights compositional change in the microstructure. Various components of the microstructure have been labeled and their composition is shown in the table below the figure. All of the microstructure does not show this much inhomogeneity, however, the inhomogeneity of the elementally blended matrix material may contribute to the deterioration of mechanical properties.

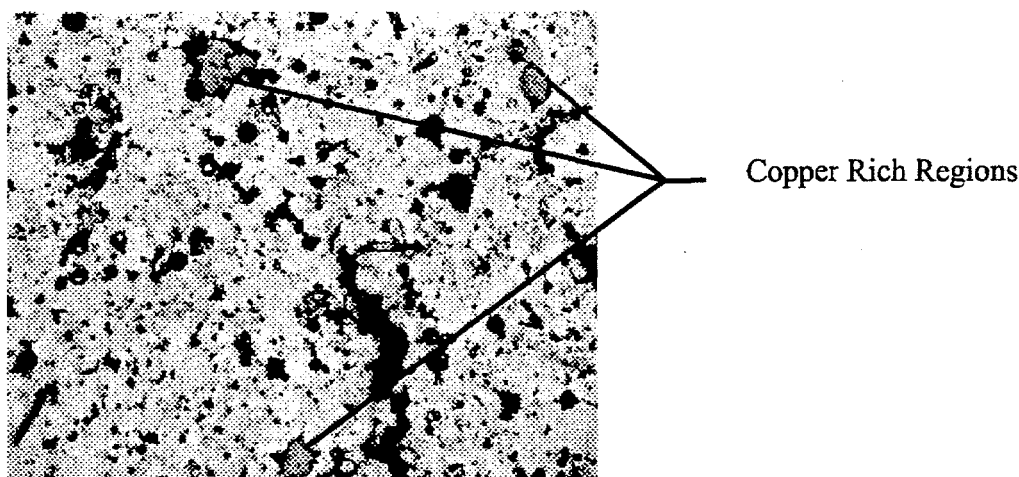
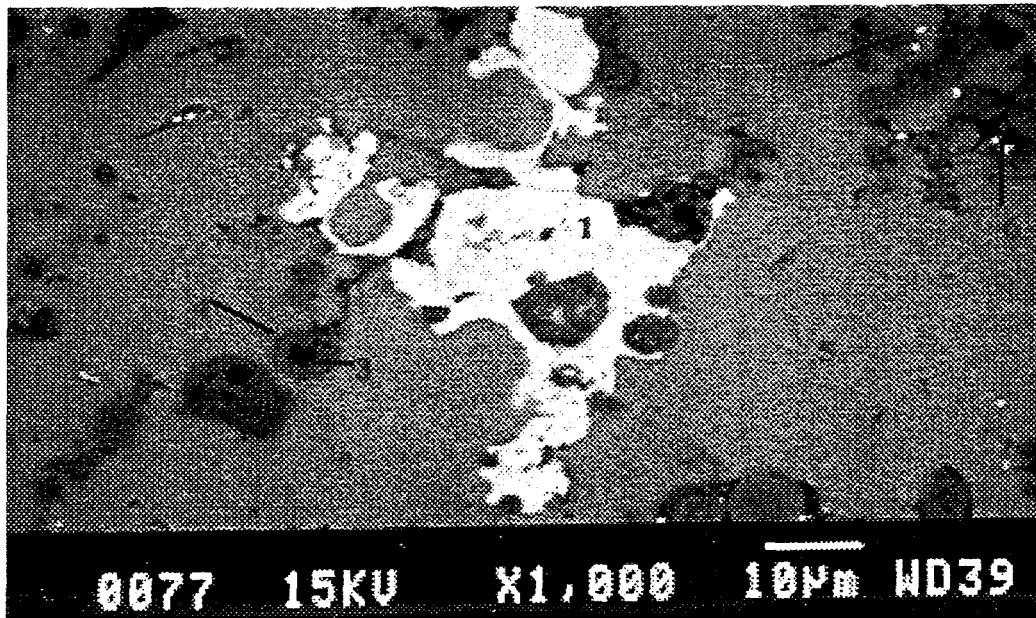


Figure 9. Microstructure of 2124 10 v/o Fly Ash (100X)

Figure 10. 2124 20 v/o Fly Ash Elemental Composition of Microstructure
(Backscattered Electron Image (BEI) at 1000X)



Microstructure Identifier (1-7 on photograph) and Wt% Composition

	1	2	3	4	5	6	7
Al	56.43	35.86	95.48	80.00	93.48	28.49	51.17
Mg	0.27	1.37	0.80	0.68	0.41	3.77	3.26
Si	10.71	48.36	1.20	5.24	0.97	0.79	6.79
S	0.00	0.00	0.23	0.18	0.00	0.67	0.42
K	0.00	4.66	0.25	4.27	0.22	0.00	0.11
Ca	0.00	3.16	0.56	0.96	0.00	0.30	0.13
Mn	14.58	0.27	0.00	0.00	0.00	0.35	0.00
Fe	12.79	0.00	0.00	0.53	0.17	0.80	0.00
Ti	0.10	0.43	0.00	0.00	0.17	0.17	0.00
Cu	5.13	4.21	0.00	7.99	4.74	64.28	38.13

Mechanical properties of the material HIP'ped at 560°C are listed in Table 6 below:

Table 6. Aluminum / Fly Ash Composite Mechanical Properties				
Composition	Fabrication	Density (% theoretical)	Ultimate Strength (psi)	Elongation (%)
2124 0% fly ash	CIP / HIP	88.2	20,880	4.7
2124 10% fly ash	CIP / HIP	94.5	24,330	0.9
2124 20% fly ash	CIP / HIP	97.3	46,490	0.7
2124 20% fly ash	CIP / Sinter	88.0	18,000	1.1

While tensile properties have improved with the alternate fabrication route, properties still can be improved with pre-alloyed powder. Gas atomized rapidly solidified prealloyed 2124 will be tried during the next quarter. With prealloyed powder the hope is that the matrix will be more homogenous and that the effect of the fly ash reinforcement will be more consistent.

TASK 5.0 - MARKET AND ECONOMIC ANALYSIS

A major issue to be addressed with the analysis of market opportunities is the nature of the supply network associated with the various opportunities. This is extremely important since, it is likely that the success of a fly ash beneficiation plant will displace other materials from the marketplace. Obviously, the successful marketing of fly ash components will require a strategy cognizant of the competition.

Market activities during this quarter focussed on three main areas - the development of a systematic database of market information for various utilization opportunities for fly ash components, a fly ash beneficiation demonstration for invited private sector representatives, and preparation of trade press articles. Each of these activities are summarized below.

Comprehensive Database

The literature is replete with applications for the constituents of coal fly ash. Other than the use of ash as a cement replacement, however, most of the applications are not firmly established. This is partially a result of a lack of a systematic summary of the specification and function requirements of the various opportunities.

The literature is being systematically reviewed to construct an application/specification (functionality) matrix of opportunities. The market potentials will consist of two categories, the

first will include current markets and opportunities available or documented by others as market potentials. A second set of opportunities will be those developed as a result of the current project.

Beneficiation Demonstration

The first of a series of demonstrations of the fly ash carbon separation by froth flotation was held at the Institute of Materials Processing's pilot plant on September 26, 1996. Representatives from three utilities, a cement company, and an ash broker were in attendance.

The demonstration was followed by a discussion of how the technology would fit into the utility industry. Much practical information was gained. It was clear from the session that the regulated history of the industry coupled with uncertainty of future environmental regulations and transition of the industry to a more unregulated competitive business climate necessitates public investment if this froth flotation technology is to be reduced to practice in the near future. Such an investment in a demonstration facility would be based on the technology's anticipated contribution to public goals of CO₂ reduction, other environmental benefits, and job creation. The data necessary to make such a decision is being documented.

Trade Press Articles

As the utility industry, and others likely to benefit from the commercialization of fly ash beneficiation, become aware of froth flotation and the success of the current project, the trade press becomes more demanding for information. This was partially satisfied by the announcement of the licensing agreement between Mineral Resources Technology (MRT) and Michigan Technological University, but the demand for more definitive information increases daily. The pilot plant demonstrations are partially designed to address this issue, but additional materials are in preparation to be sent directly to the trade press.

Economic Information

We have preliminary quotes from vendors on capital costs for the primary commercial scale equipment. This has allowed us to further refine the overall capital costs of plants ranging from 15 tph to 50 tph. In addition to the major pieces of equipment being quoted, ancillary items (such as materials handling and controls) are also included. Factors were also generated to account for the controls and installation of each of the primary pieces of equipment.

Operating costs are also being generated to address the anticipated manpower, maintenance, and utilities that would be required to operate a commercial plant at the levels given previously.

APPENDIX B

Invitation to the MRT/MTU Carbon Removal Process Demonstration

ANNOUNCEMENT

Fly Ash Carbon Removal System Presentation & Demonstration

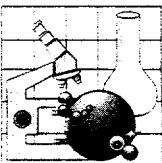
Presented by

**Michigan Technological University
(MTU)**

and

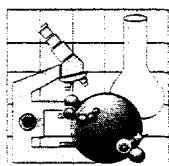
**Mineral Resource Technologies, LLC
(MRT)**

- Meeting Date September 26, 1996
 9:00 a.m. - 2:30 p.m.
- Location Michigan Technological University
 1400 Townsend Drive
 Houghton, Michigan 49931
 Institute of Material Processing
- Accommodations Best Western Franklin Square
 (906) 487-1700
 A block of rooms have been reserved in MRT's name,
 ask for MRT group rate (\$57.00 + tax)
- Airlines Houghton, Michigan is serviced by Northwest Airlines
 with flights from Minneapolis and Detroit.
- Note Due to limited facility space and limited available air
 transportation, attendance will be restricted to about 30
 people. Please call Richard Basaraba at (770) 989-0089
 to reserve attendance for yourself prior to making any
 reservations.



**Information And
Advantages Of The Patented Carbon
Removal System Offered By
The MTU/MRT Process**

**Mineral Resource Technologies, LLC
120 Interstate North Parkway East
Suite 440
Atlanta, GA 30339
Phone: (770) 989-0089
FAX: (770) 989-0079**



FLY ASH BENEFICIATION FOR CARBON REMOVAL AND POZZOLAN ENHANCEMENT

Process - A patented process (U.S. Patents 5,047,145 and 5,227,047) has been developed and advanced by Michigan Technological University for the beneficiation of coal fly ash. Froth floatation is used to remove carbon and enhance fly ash. Mineral Resource Technologies, LLC, has the exclusive patent rights for commercialization and development of facilities to produce enhanced pozzolan and marketable carbon.

The wet process for beneficiation of a fly ash by-product has the following selected steps:

a) forming a slurry mixture of a fly ash material and a liquid; b) gravitationally separating and collecting a first material fraction of the fly ash having a density less than the liquid by skimming off floatation slurry material; c) separating the unburned carbon from the remaining slurry components by adding an effective amount of an oil having a carbon chain greater than octane, and frothing agent whereby the oil coats the unburned carbon forming hydrophobic carbon materials and inducing air into the system for frothing the slurry mixture wherein the hydrophobic unburned carbon froths to the surface and is removed by skimming off the frothing layer; and d) collecting the remaining fraction of fly ash. The products are dewatered and dried for shipment to respective markets.

Equipment Systems - The carbon removal wet processing facility consists of fly ash raw feed silos, wet condition slurry system, primary and secondary floatation cells, dewatering equipment, drying equipment, conveying systems, finished product storage silos and loadout equipment.

The liquid portion of this process is very close to a closed loop system. Water discharges are kept to a minimum. A small amount of make-up water is required to replace water evaporated in the drying process.

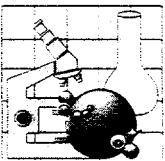
The system is adjustable to accommodate and match up with certain existing plant equipment. This can lead to substantial cost savings of purchased equipment and operating cost.

Plants generally can be designed to accommodate any annual fly ash production rate, from low volume to very high volume. Plants can be designed with production rates as low as 5 tons per hour to as high as 80-100 tons per hour.

Construction Requirement - Construction of the carbon removal wet processing facility can vary depending upon the utilization of existing equipment. Often it is practical to use the existing storage silos and conveying systems for the raw feed system into the wet process. Existing facilities may also allow storage for the finished products. Electrical power and fuel, natural gas or propane are the two major energies required.

Depending on the size and the layout of the existing plant, a plant footprint of one half acre to approximately three acres are required to accommodate the carbon removal plant. The carbon removal plant is enclosed to allow for year round operation.

A typical carbon removal plant will require from eight months to 15 months to complete, after siting requirements are finalized.



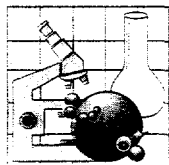
Information and Advantages of the Patented Carbon Removal System Offered by MTU/MRT

Process Advantages

- Wet floatation is a well understood and proven technology that has been used by the minerals processing industry since the turn of the century. Floatation is currently used in the coal industry and in the production of Kaolin. Most of the major minerals are processed in this manner.
- The MTU/MRT patented process (U.S. Patents 5,047,145 and 5,227,047) incorporates the best of wet floatation, advancement and development of conditioning agents, dewatering, and drying technology to provide high recovery rates of both a high grade carbon and fly ash.
- The MTU/MRT process is a system that will consistently and routinely reduce carbon in both low and very high fly ashes down to a level of 1% or less in an effective and efficient manner. The process can handle variable L.O.I. ash better than dry separation.
- The MTU/MRT system produces the optimum product. This system, even at high hourly throughput can produce a beneficiated pozzolan with 1% or less carbon at a 90% or greater recovery rate. Carbon is produced at a 80% purity level, which may be further processed if desired. The dry systems can not reach these high purity and recovery rates.
- Dry processes that reduce carbon in fly ash by 50 to 55% still produce an inferior product, especially if the final product L.O.I.'s are variable. Fly ashes above 8% L.O.I. also are not helped by a 50% reduction.
- The MTU/MRT system also may be designed to recover cenospheres and magnetite, should economics and available quantity justify.
- Total operating cost, including capital costs, are estimated between \$6.00 and \$12.00 per ton. The range is a result of many variables, such as; the required plant size, production rates, climate, production days per year, etc. Also, where existing equipment, such as, silos for storage of finished products and load out facilities are available, capital cost could be lower, reducing overall operating cost.

Product Advantages

- The patented MTU/MRT process, removes a mineral called Basanite (CaSO_4) from the surface of the fly ash. Basanite is a Gypsum like material that has a retarding effect on cement in concrete mixtures. The removal via wet processing improves early set and strength in concrete. This benefit does not occur with a dry process.
- The patented MTU/MRT process produces a consistent enhanced pozzolan product ready mix producers desire. A carbon content of 1.0% or less has virtually no effect on entrained air in concrete. A carbon content of approximately 3%, for example, has a dramatic effect on air entrained concrete.



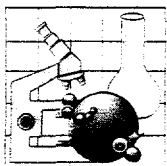
- The ash produced by the patented MTU/MRT process can be utilized as is for higher value applications because of its high quality and consistency. The ash can be further processed for even higher value uses. Some of these include uses for industrial fillers for plastics, rubber and specialty applications.
- The carbon product produced by the MTU/MRT process has a purity of 80% or greater with multiple application potential that clearly sets it aside from other processes.
- The patented MTU/MRT wet floatation process is equally effective in removing all of the different types of carbons in the ash. Recent data indicate that some dry separation processes remove more graphitic carbon, which is less adsorbent than carbon produced by our process.
- The byproduct carbon produced by the patented MTU/MRT process has a value based upon a number of market areas, including at the least, as a high BTU fuel. Current market research indicate the carbon produced by the MTU/MRT process should be able to be used in traditional markets, such as, purification and activated carbon.
- The high purity carbon has the potential to remove mercury and other heavy metals from gas streams at coal-fired plants. This carbon may also be used to treat disposal water from power plants, including discharge effluents.

Environmental Advantages

- Another wet process uses kerosene for conditioning. Kerosene is expensive, since the demand per ton is high, and leaves an odor in both the enhanced pozzolan and the carbon. The removal of water laden with small quantities of kerosene also poses environmental problems in the drying phase of the process. The patented MTU/MRT process uses low doses of conditioning agents which are very effective, efficient and most importantly, environmentally friendly.

For further information on the process, please contact Richard Basaraba at (770) 989-0089, FAX: (770) 989-0079.

Mineral Resource Technologies, LLC
120 Interstate North Parkway East, Suite 440
Atlanta, Georgia 30339

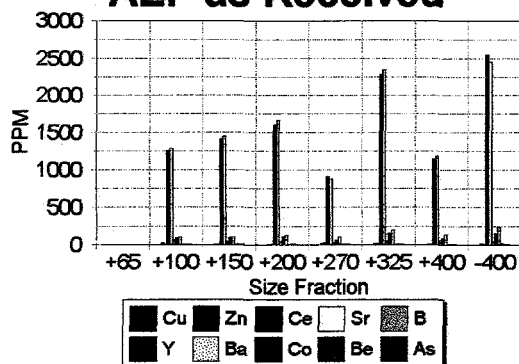


APPENDIX C

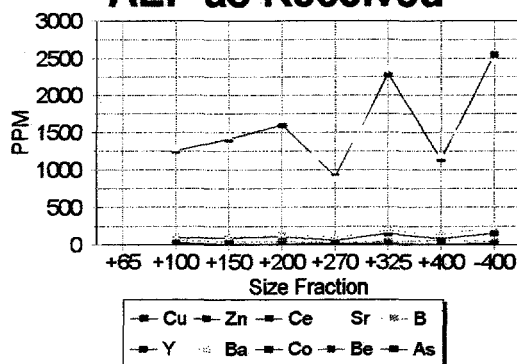
Task 2.2 - Material Characterization

Trace Element and Water Chemistry Analytical Results

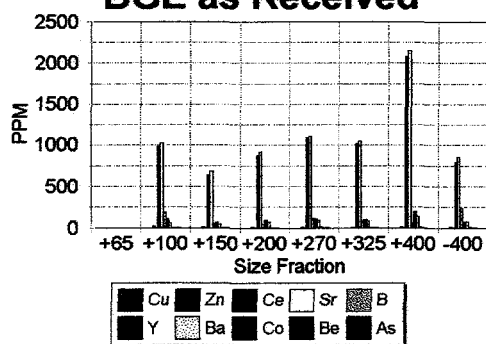
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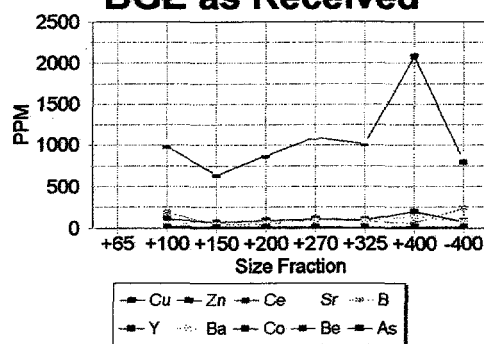
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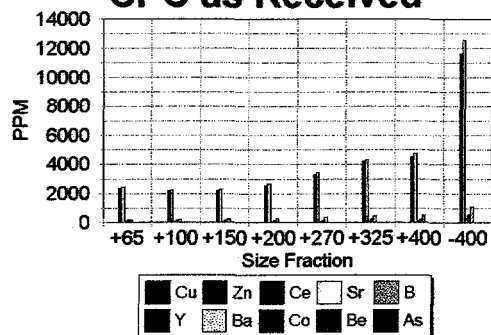
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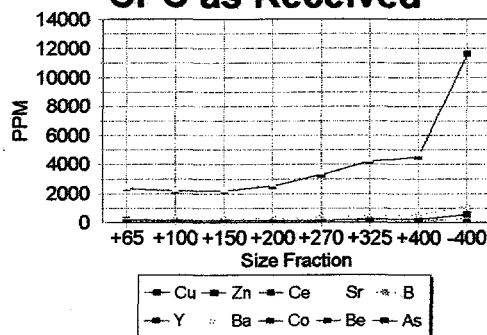
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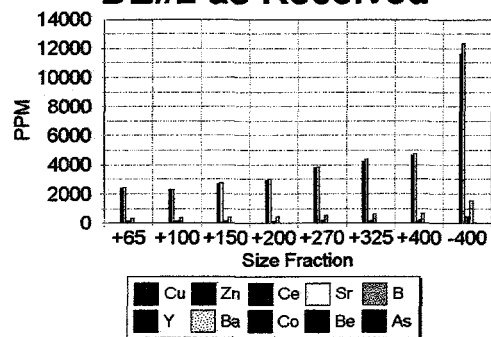
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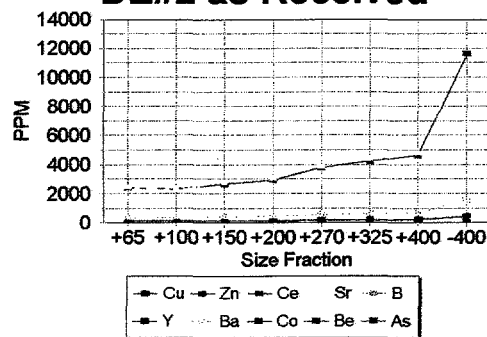
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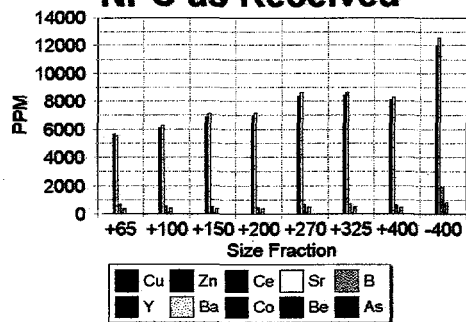
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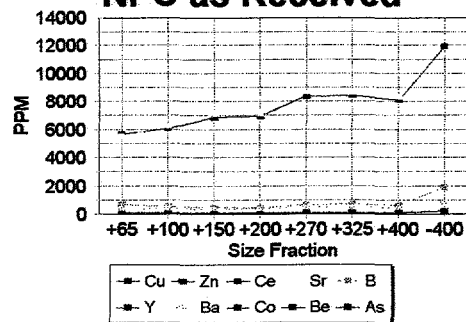
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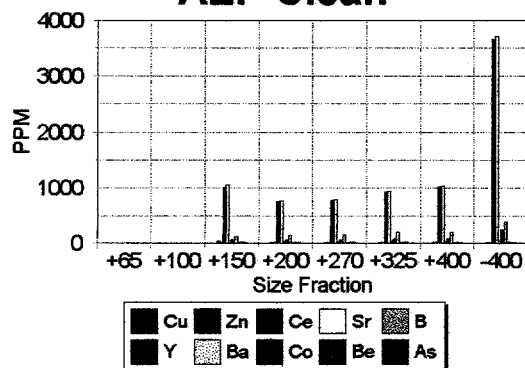
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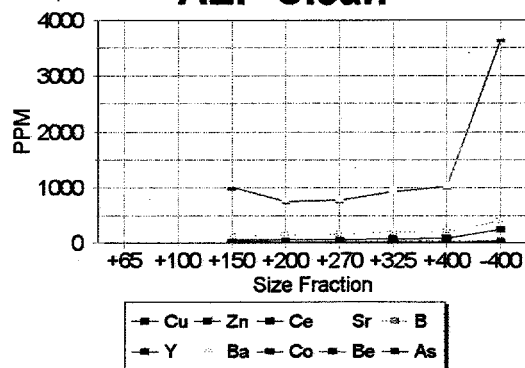
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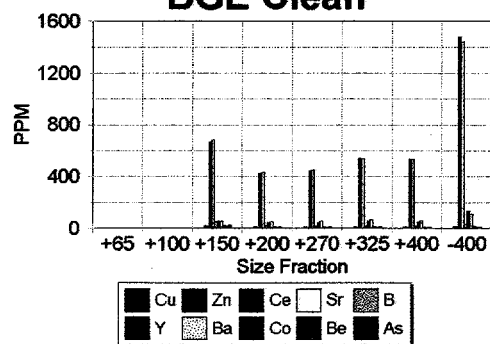
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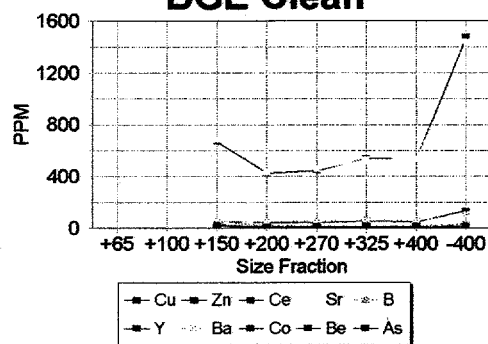
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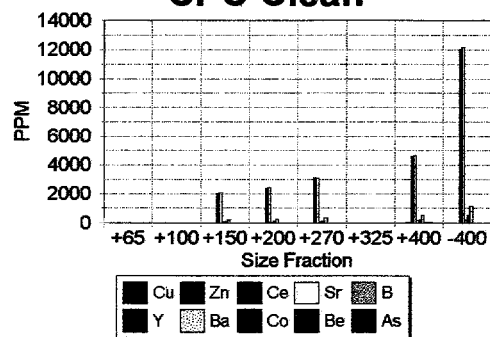
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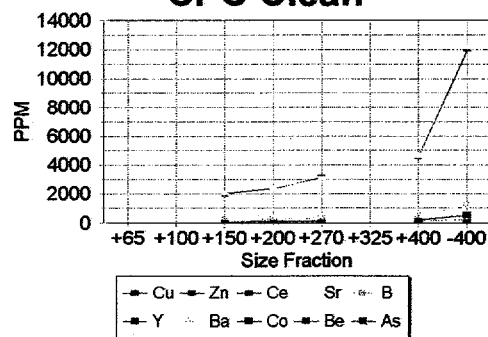
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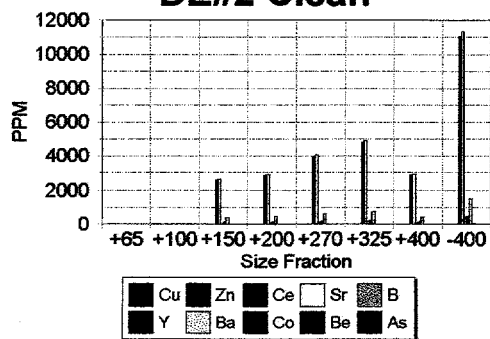
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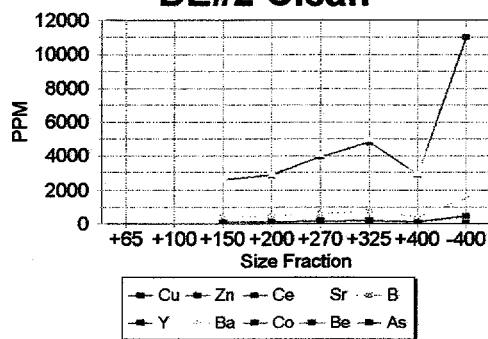
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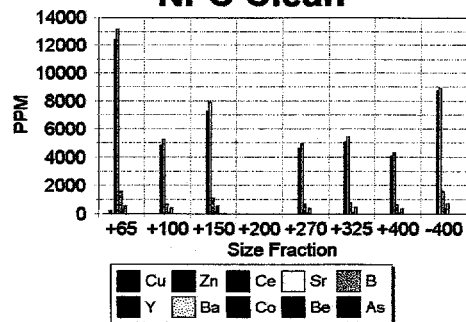
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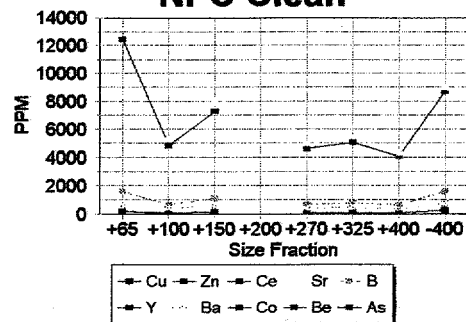
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NPC Clean



WATER ANALYSIS - CLASS C FLY ASH

Contaminant	Drinking Water Standards Maximum Contamination Level (mg/L)	Carbon Stream (mg/L)	Clean Ash Stream (mg/L)	Fresh Water (mg/L)
Aluminum	0.05 - 0.2	0.24	0.42	0.55
Antimony	0.006	0.03	0.06	0.07
Arsenic	0.05	< 0.053	< 0.053	< 0.053
Barium	1.0	1.08	1.66	0.07
Beryllium	0.004	< 0.00027	< 0.00027	< 0.00027
Cadmium	0.005	< 0.0025	< 0.0025	< 0.0025
Chromium	0.1	0.38	0.18	< 0.0071
Copper	1.0	0.03	0.08	< 0.01
Iron	0.3	0.31	0.4	0.04
Lead	0.05	< 0.042	< 0.042	< 0.042
Manganese	0.05	< 0.0014	< 0.0014	0.06
Mercury	0.002	< 0.025	< 0.025	< 0.025
Nickel	0.1	0.02	0.04	< 0.01
Selenium	0.05	0.23	0.31	< 0.075
Silver	0.1	0.01	0.01	0.02
Thallium	0.002	0.17	0.14	0.25
Zinc	5	1.09	1.95	0.29

WATER ANALYSIS - CLASS F FLY ASH

Contaminant	Drinking Water Standards Maximum Contamination Level (mg/L)	Carbon Stream (mg/L)	Clean Ash Stream (mg/L)	Fresh Water (mg/L)
Aluminum	0.05 - 0.2	0.1	2.4	0.55
Antimony	0.006	< 0.032	< 0.032	< 0.032
Arsenic	0.05	< 0.053	< 0.053	< 0.053
Barium	1.0	0.17	0.19	0.05
Beryllium	0.004	< 0.00027	< 0.00027	< 0.00027
Cadmium	0.005	< 0.0025	< 0.0025	< 0.0025
Chromium	0.1	< 0.01	< 0.0071	< 0.0071
Copper	1.0	< 0.0054	< 0.0054	< 0.0054
Iron	0.3	< 0.0046	0.07	0.03
Lead	0.05	< 0.042	< 0.042	< 0.042
Manganese	0.05	< 0.0014	< 0.0014	0.07
Mercury	0.002	< 0.025	< 0.025	< 0.025
Nickel	0.1	< 0.01	0.16	< 0.01
Selenium	0.05	0.25	0.09	< 0.075
Silver	0.1	0.01	0.02	0.02
Thallium	0.002	< 0.040	< 0.040	< 0.040
Zinc	5	0.39	3.04	0.1

WATER ANALYSIS - CLASS C/F MIXTURE FLY ASH

Contaminant	Drinking Water Standards Maximum Contamination Level (mg/L)	Carbon Stream (mg/L)	Clean Ash Stream (mg/L)	Fresh Water (mg/L)
Aluminum	0.05 - 0.2	8.72	41.67	< 0.023
Antimony	0.006	< 0.032	< 0.032	< 0.032
Arsenic	0.05	< 0.053	< 0.053	< 0.053
Barium	1.0	0.17	0.10	0.06
Beryllium	0.004	< 0.00027	< 0.00027	< 0.00027
Cadmium	0.005	< 0.0025	< 0.0025	< 0.0025
Chromium	0.1	0.17	0.60	< 0.0071
Copper	1.0	< 0.0054	< 0.0054	< 0.0054
Iron	0.3	< 0.0046	< 0.0046	< 0.0046
Lead	0.05	< 0.042	< 0.042	< 0.042
Manganese	0.05	< 0.0014	< 0.0014	0.06
Mercury	0.002	< 0.025	< 0.025	< 0.025
Nickel	0.1	0.03	0.03	0.03
Selenium	0.05	0.45	0.97	< 0.075
Silver	0.1	0.01	0.01	0.01
Thallium	0.002	< 0.040	0.09	< 0.040
Zinc	5	0.90	< 0.0018	0.12

APPENDIX D

Task 4.1 - Concrete Testing

“Utilization of Beneficiated Low NO_x Fly Ash in Concrete and Concrete Block”

for presentation at

**ACAA's 12th International Symposium on Management & Use of Coal Combustion
Byproducts, Orlando, Florida, January 26-30, 1997**

UTILIZATION OF BENEFICIATED LOW NO_x FLY ASH IN CONCRETE AND CONCRETE BLOCK

X. Michael Song

and

Jiann-Yang Hwang

and

Xian-Ping Liu

Institute of Materials Processing
Michigan Technological University
1400 Townsend Drive
Houghton, Michigan, USA 49931-1295

Abstract

A class F ash, from low NO_x burner of American Electric Power Company (AEP), has an average LOI value of 21.7%, much higher than the ASTM 618 limit for concrete use. The as-received ash was beneficiated to separate carbon, cenospheres, and magnetic materials, that make up about 25% of the total weight of the ash. The remaining 75%, termed cleaned AEP ash, is mainly composed of silicate sphere, and a few irregular solids. After separation, the average LOI of the cleaned ash was reduced to 0.4%. Both as-received and cleaned fly ash were used to partially replace cement in manufacturing concrete and concrete blocks. For the concrete containing cleaned ash, the air content averaged 6.3% (in a 3.5 ksi specific design strength) in comparison to 7% in concrete made without the fly ash, and 1.9% made with as-received ash. To obtain the desired slump value, the water to cementitious materials ratio decreases as the cleaned fly ash replacing cement increases; when as-received ash is used, the ratio increases. The concrete formed with both as-received and cleaned fly ash replacing up to 30% of the cement for a 3.5 ksi specific design strength meets compressive strength specifications. The effects of LOI content on concrete workability and strength, and the effect of the amount of cement replaced by fly ash in varied specific strength design were discussed. Concrete blocks containing as-received or cleaned fly ash were manufactured and the quality of the block was analyzed.

Introduction

Fly ash presents a serious solid-waste disposal problem in the United States. Approximately 50 million tons of fly ash are generated annually nationwide, and more than 78% of these materials are disposed in landfills (1, 2). Due to the increase of fly ash disposal costs and the shortage of valid landfills, an increased interest has been shown from industries to enlarge the utilization rate of fly ash. The problem is that fly ash quality varies with combustion equipment, plant operation conditions, coal types and their composition, as well as fly ash collection methods, which limits its application (3).

The cement and concrete industry is the largest market for fly ash. More than 70% of the total collected fly ash is used in manufacturing concrete products; other uses include soil stabilization and asphalt filling, etc. The critical specification of fly ash for concrete use in ASTM C 618 limits the LOI value less than 6% because high LOI increases the consumption of water and air entraining, affects workability of fresh concrete, and stains the concrete (3, 4). In practical manufacturing, contractors prefer an LOI value as low as possible, such as 3% or lower. Unfortunately, most fly ash from power plants can not meet the ASTM C 618 standard.

A beneficiation process for fly ash has been successfully developed by the Institute of Materials Processing, Michigan Technological University. This process can sufficiently control the quality of the fly ash by choicely separating some constituents from fly ash such as carbon, cenospheres, and iron oxide microspheres (5). After separation, the remaining product referred to as cleaned ash has a consistent low LOI value which meets ASTM C 618-92 specification.

The objectives of this study were to utilize both as-received and cleaned ash in manufacturing the concrete and concrete blocks, and to evaluate their properties. Specific areas addressed included:

- Characterization of as-received and cleaned fly ash;
- Performing fresh fly ash-cement-water mixture;
- Mechanical properties of the concrete;
- Physical and mechanical properties of concrete block.

Materials and Methods

A low NO_x class F ash with an average LOI value of 21.7% was provided by Glen Lyn Plant, American Electric Power Company (AEP). The as-received AEP ash was separated by beneficiation process to recover carbon, cenospheres, and magnetic materials, which is about 25% of total weight of the ash. The remaining 75%, termed cleaned AEP ash, was mainly composed of silicate sphere, and a few irregular solids. Both as-received and cleaned AEP ash were used to make concrete in our laboratory and to manufacture normal weight concrete blocks in Concrete Testing Lab, Alpena, MI.

In making concrete, commercially produced Type 1 cement and a Grace Daravair air entraining agent were used. The dosage for the air entraining agent was about 1.8 oz per 100 lb of cementitious materials for the both as-received and cleaned ash concrete. Coarse aggregate size distribution followed: 4% retained on 1" sieve, 60% retained on 0.5" sieve, and 36% passed 0.5"

sieve, which meets ASTM C 33. The specific gravity and absorption of the aggregates were 2.70 and 1.6, respectively. Fine aggregates (2NS sand) had a 2.66 specific gravity and a 1.0 absorption. All the aggregates were stored at room temperature for one week prior to making concrete. All concrete mixtures were prepared using a portable concrete mixer with a batch capacity of 2.5 cubic feet. The procedure for making concrete follows ASTM C 192, making and Curing Concrete Test Specimens in the Laboratory (6).

The concrete was designed to be Grade 35S, ie. a commonly used concrete with compressive strength of 3,500 psi at 28 days (7). The design is based on the absolute volume method (8). In this experiment design, the amount of cement replaced by the fly ash, based on the total weight of cement, was 8, 20, and 30%, respectively. The concrete for Grade 35S without fly ash was also made and used for comparison purpose. In order to understand the effect of fly ash on varied grade's concrete, the concrete was also designed to be Grades 30S and 40S following above the experiment (7). The amount of cement replaced by the fly ash in the experiment, based on the total weight of the cement, was 20, and 30%. The concretes for Grades 30S and 40S without fly ash were also made for comparison purpose.

Fresh cement paste tests included slump, air content, and density. Nine standard cylindrical specimens from each batch were prepared for compressive strength tests. Three cylinders were tested at 7 day, 28 day and 91 day, respectively following ASTM C116 test method (9).

In manufacturing normal weight concrete blocks, V3-12 Besser Block Machine was used to make 8 x 8 x 6 inch blocks; each block had two hollows, and each batch made 68-72 blocks. Commercially produced Type 1 cement, 2NS fine aggregate, and 3IC coarse aggregate were used in block manufacturing. In the experiment design, the amount of cement replaced by cleaned ash, based on the total weight of cement, was 15, 20, and 30%, respectively. The amount of cement replaced by as-received AEP ash was 20%. The concrete block without fly ash was also made and used for comparison purpose. All the tests followed ASTM C140 standard methods (10).

Results and Discussion

Characterization of As-received and Cleaned Ash

Table 1 shows the results of chemical composition and physical properties of as-received and cleaned AEP ash. From Table 1, the LOI value was reduced from 21.7% to 0.4% after separation. SiO_2 and Al_2O_3 increased from 44.4 and 22.4% to 58.6 and 29.2%, respectively. CaO showed a slight increase from 0.76 to 0.85 after separation. The physical testing results indicate that moisture content decreased from 0.25 to 0.20, and specific gravity increased from 2.13 to 2.19 after separation.

The AEP ash size was analyzed by Tyler Mesh and Microtrac Analyzer, and the results were recorded in Tables 2 and 3, respectively. From Table 2, the particle size significantly decreased after separation. The cleaned ash passing 400 mesh was 70.45% in comparison to 53.83% of as-received ash passing the same size sieve. The fly ash particles passing 400 mesh were further analyzed by Microtrac Analyzer, and the results (Table 3) indicate that the finer particles in cleaned ash were

much more than that in as-received ash.

The microscopic structures of as-received and cleaned AEP fly ash were observed by scanning electron microscopy (SEM). Figure 1 shows that the as-received ash consisted of amorphous and sphere particles. The amorphous particles were large in size, whereas the sphere particles were small in size. Energy dispersive spectroscopy (EDS) tests indicate that the amorphous particles were composed of 45-77% SiO_2 , 15-23% Al_2O_3 , 3-4.5% iron oxide, and trace elements. The sphere particles were composed of 55% SiO_2 , 33% Al_2O_3 , 1.5-3.0% iron oxide, and trace elements. Figure 2 shows that the cleaned ash was also composed of amorphous and sphere particles, but the amount of amorphous particles was less and the size was smaller than the as-received AEP ash. The chemical composition for amorphous and sphere particles in cleaned AEP ash was the same as the as-received AEP ash.

Performing Fresh Ash-cement-water Mixture

Tables 4 shows the water requirement, workability of fresh fly ash-cement-water mixture and compressive strength of the concrete. The water to cement ratio was designed at 0.5 for Grade 35S concrete. When the as-received ash was used to replace cement, the water to cementitious material ratio increased with the amount of cement replaced by the ash in order to obtain desired slump value. In contrast with the as-received ash, the water to cementitious material ratio decreased with the amount of cement replaced by the cleaned ash in order to obtain desired slump value.

The high water requirement of as-received ash-cement-water mixture is mainly due to the high LOI content in the ash because carbon particles with porous structure can absorb more water. Increasing the amount of cement replaced by the ash, the carbon particles in unit volume increase, therefore the water requirement enlarges in order to obtain desired slump. When the LOI content is reduced by beneficiation processing, the water requirement of cleaned ash-cement-water mixture is reduced as the cleaned ash fraction increases, which improves cement workability. Differences in particle size distribution and shape between as-received and cleaned fly ash may be another factor influencing water requirement in concrete paste. The high proportion of fine and smooth spherical shapes of particles in the cleaned ash may persist in improving rheological properties of fresh concrete paste.

The air content in fresh cement paste without fly ash was 7.1%. When the as-received ash was added, the air content was reduced to 2% or less. When the LOI content was reduced by beneficiation process, the air content in the cleaned ash-cement-water mixture had an average 6.3 % for grade 35S concrete, and an average 6.5 % for grade 30S concrete. The air content in cleaned ash-cement-water mixture for grade 40S was higher than the fresh cement paste without fly ash.

All the fresh concrete mixture entraps a certain amount of air during mixing. The entrained air can improve the flow properties and workability of the fresh cement mixture. When the as-received ash was added into the mixture, the loss of air may relate to the high content of carbon particles in the ash because of their high specific surface area and sorption capacity. The low air in the as-received ash-cement-water mixture increases the requirement of water for flow of the cement.

In order to keep a equal level of air in the ash-cement-water mixture as the concrete without ash, the air entraining agent has to be added at a much higher amount than the usual amount (11). When the LOI content is reduced by beneficiation process, the air content in the cleaned ash-cement-water mixture is only slightly decreased in grade 35S concrete in comparison to the fresh concrete without fly ash.

Mechanical Properties of the Concrete

Figure 3 shows the effects of the amount of cement replaced by fly ash and the curing period on compressive strengths of Grade 35S concretes. The concrete with 8% as-received ash had the high 7 day compressive strength and the concretes with 20 and 30% as-received ash had the low 7 day compressive strengths in comparison to the concrete without fly ash. All the concretes with cleaned ash had lower 7 day compressive strengths than the concrete without fly ash. The 28 day compressive strengths of both as-received and cleaned ash concretes were over 3500 psi, which satisfies the design requirement. The 91 day compressive strengths of the concretes including both 8 and 20% as-received and 8% cleaned ash were, respectively, 6902, 6201, and 6025 psi, those are higher than the strength of concrete without fly ash (5512 psi). The 91 day compressive strengths of the concretes with 20 cleaned ash was 5442, which is nearly same as the strength of the concrete without fly ash.

Compared to the concrete without fly ash, the concrete with fly ash has a low early strength except the concrete with 8% as-received fly ash. The concrete with fly ash has a fast development of strength during day 28 to 91 in comparison to the concrete without fly ash. Comparing the concrete with as-received fly ash, the concrete with cleaned ash has relatively low compressive strengths for all ash level and curing period. The reason of this is not clear. From the microstructure of fly ash, the cleaned ash, with more fine and smooth particles, assists in the strength development of the concrete which has been proven by previous studies (12, 13). From the ratio of water to cementitious material, a low water requirement for the cleaned ash-cement-water mixture would improve the compressive strength of the concrete. A possible reason is the change of ash composition which affects the reaction between the cleaned ash and cement. Further studies need to be conducted to examine the surface activity and polarity of fly ash as well as any chemical reaction existing between the fly ash and cement.

Figure 4 shows compressive strengths of grades 30S, 35S and 40S concrete with and without cleaned fly ash. All the grades of concrete with cleaned ash had the lower 7 day compressive strengths than the same grades of concrete without fly ash. The 28 day compressive strengths of concrete with 20% cleaned ash met the designed requirement for all three grades of concrete. Only the grade 35S concrete with 30% of the cement replaced by the cleaned ash satisfied compressive strength specifications. The concrete with clean ash had a fast development of strength during 28 to 91 days for all three grades in comparison to the concrete without fly ash. The 91 day compressive strengths of grade 30S concrete including 20% cleaned ash was 4547 psi which is higher than the strength of concrete without fly ash (4399 psi). The 91 day compressive strengths of grade 35S concretes with 20 cleaned ash was 5442, which is nearly the same as the strength of the concrete without fly ash (5512 psi). The 91 day compressive strengths of grade 40S concretes with

20% cleaned ash was 5204, which is close to the strength of the concrete without fly ash (5412 psi).

Physical and Mechanical Properties of concrete blocks

Table 5 shows the density, moisture content, absorption, and compressive strength of concrete blocks with various curing period.

Figure 5 shows the effects of fly ash type, amount of cement replaced by fly ash, and curing period on compressive strengths of concrete blocks. All the concretes with fly ash had lower compressive strengths than the concrete without fly ash throughout all the curing periods. All the concrete with cleaned ash had the lower 1 day compressive strength than the concretes with 20% as-received ash. The concrete with cleaned ash has a fast development of the strength during 1 to 7 day in comparison to the concrete with as-received ash. The concretes with 15 and 20% cleaned ash had higher 7 day compressive strengths than the concrete with 20% as-received ash. The 28 day compressive strengths of both as-received and cleaned ash concretes met designed requirement.

Conclusions

Several conclusions can be drawn from the study:

1. A class F fly ash with a LOI value of 21.7 could not meet the ASTM C 618 limit for concrete use. The beneficiation process was employed to separate carbon, cenospheres, and magnetic materials from the as-received ash, which reduced the LOI value to 0.04% and satisfied the ASTM requirement.
2. After separation by beneficiation process, other changes of chemical composition include: SiO_2 increased from 44.4 to 58.6; Al_2O_3 increased from 22.4% to 29.2%; CaO was slightly increased from 0.76 to 0.85.
3. From the analysis of fly ash size and microstructure, the particle size was significantly reduced after separation, and small particles contained a large proportion of cleaned ash in comparison to the particles in as-received ash. Scanning electron micrographs proved that both as-received and cleaned ash were composed of amorphous and sphere particles, but the amount of amorphous particles in the cleaned ash was less and the size was smaller than the as-received ash.
4. In fresh concrete paste, water to cementitious material ratio increased with the amount of cement replaced by the as-received ash in order to obtain the desired slump value, whereas the water to cementitious material ratio decreased with the amount of cement replaced by the cleaned ash. Air content in the mixture greatly decreased as the as-received fly ash was added. The air content in the mixture decreased only slightly as the cleaned fly ash was added.
5. The concrete with the fly ash had a lower early strength than the concrete without fly ash except the concrete with 3% as-received fly ash. The concrete with the fly ash has a fast development of strength during the 28 to 91 day curing period in comparison to the concrete without fly ash.

The concrete formed with either as-received and cleaned fly ash replacing up to 30% of the cement for a 3.5 ksi specific design strength mixture meets compressive strength specifications.

6. Similar to the concrete, the concrete blocks with fly ash had a lower early strength than the concrete without fly ash. The concrete blocks formed with either as-received and cleaned fly ash replacing up to 30% of the cement meets the 28 day compressive strength specifications.
7. In comparison to as-received ash, the concrete containing cleaned ash has advantages such as good workability, better general appearance, lower water to cementitious materials ratio, higher air contents at the same slump values, and the 28 day compressive strengths meet the requirements.

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Table 1
Chemical composition and physical properties of as-received and cleaned ash

Chemical Composition	As-received fly ash %	Cleaned fly ash %	ASTM C 618 (Class F ash)
Al_2O_3	22.4	29.2	
SiO_2	44.0	58.6	
Fe_2O_3	5.3	5.2	
<i>Total $SiO_2 + Al_2O_3 + Fe_2O_3$</i>	71.7	93.0	70 (minimum)
CaO	0.76	0.85	
MgO	0.86	1.11	
Na_2O	0.32	0.42	
K_2O	2.35	3.16	
TiO_2	1.11	1.33	
P_2O_5	0.03	0.09	
LOI	21.7	0.40	6.0 (maximum)
Total	98.8	100.4	
Physical properties			
Moisture content (%)	0.25	0.20	3.0 (maximum)
Specific gravity (g/cm^3)	2.13	2.19	

Table 2
Particle size and distribution of as-received ash and cleaned AEP fly ash

Tyler Mesh	As-received ash			Cleaned ash		
	Weight %	Individual %	Cumulative %	Weight %	Individual %	Cumulative %
+65	0.60	0.77	0.77	0.00	0.00	0.00
+100	1.40	1.79	2.55	0.00	0.00	0.00
+150	4.20	5.36	7.91	0.60	1.36	1.36
+200	7.80	9.95	17.86	2.40	5.45	6.82
+270	8.00	10.2	28.06	2.80	6.36	13.18
+325	3.80	4.85	32.91	4.00	9.09	22.27
+400	10.4	13.3	46.17	3.20	7.27	29.55
-400	42.2	53.8	100.0	31.0	70.45	100.0

Table 3
Microtrac analysis of particle size distribution for fly ash passing 400 mesh

Channel	As-received ash		Cleaned ash	
	Cumulative %	Volume %	Cumulative %	Volume %
62	100.0	5.2	99.9	4.3
44	94.8	15.2	95.5	12.1
31	79.6	18.1	83.5	14.7
22	61.5	16.2	68.8	14.3
16	45.3	14.3	54.5	13.9
11	31.0	10.9	40.6	11.8
7.8	20.1	8.2	28.8	9.4
5.5	11.9	5.1	19.4	6.6
3.9	6.8	3.2	12.7	5.4
2.8	3.6	2.7	7.4	4.8
1.9	0.9	0.7	2.6	1.7
1.4	0.2	0.2	0.8	0.8
0.9	0.0	0.0	0.0	0.0

Table 4
Effects of amount of cement replaced by fly ash and curing period on concrete properties

Concrete grade and type		W/C ^a ratio	Slump in	Air %	Density pcf ^b	Compressive strength psi		
						7 day	28 day	91 day
Grade 35S concretes with as- received ash	0%	0.50	3.5	7.1	148.8	3692	4676	5512
	8%	0.50	3.2	2.0	151.2	4223	5801	6902
	20%	0.51	2.5	1.8	149.6	3357	4582	6201
	30%	0.52	2.2	1.9	148.9	2420	3681	5141
Grade 35S concretes with cleaned ash	0%	0.50	3.5	7.1	148.8	3692	4676	5512
	8%	0.47	3.2	6.5	145.4	3263	4446	6025
	20%	0.46	3.0	5.5	145.8	2561	3999	5442
	30%	0.44	3.5	6.9	144.2	2273	3681	4659
Grade 30S concretes with cleaned ash	0%	0.50	2.5	7.0	146.4	3474	4158	4399
	20%	0.48	4.0	7.5	145.3	2385	3186	4547
	30%	0.46	3.3	6.0	144.4	1976	2774	4076
Grade 40S concretes with cleaned ash	0%	0.47	4.0	5.5	148.4	3981	4823	5412
	20%	0.43	5.25	9.0	142.3	2609	4020	5204
	30%	0.41	4.5	6.0	144.2	2415	3822	4953

Note: a) W/C ratio is the ratio of water/(cement + fly ash).
b) The pcf is pound per cubic yard.

Table 5
Physical and mechanical properties of concrete block

Test period	Block properties	Block without fly ash	Block with 20% as-received ash	Cleaned ash content in block		
				15%	20%	30%
1 day	Density (pcf ^a)	138.2	133.0	129.0	134.3	133.9
	Moisture content (%)	37.8	23.8	21.4	24.3	16.8
	Absorption (pcf)	7.5	7.9	9.0	7.7	7.5
	Compressive strength (psi)	2260	1750	1670	1380	1320
7 day	Density (pcf)	138.2	134.5	132.8	134.3	133.9
	Moisture content (%)	37.8	28.1	27.8	24.3	24.6
	Absorption (pcf)	7.5	8.2	8.2	7.7	7.5
	Compressive strength (psi)	3120	2130	2790	2320	1930
14 day	Density (pcf)	138.2	134.3	132.8	134.5	133.9
	Moisture content (%)	37.8	24.3	27.8	28.1	24.6
	Absorption (pcf)	7.5	7.7	8.2	8.2	7.5
	Compressive strength (psi)	3310	2400	2820	2520	2280
14 day	Density (pcf)	138.2	131.0	132.8	134.3	133.9
	Moisture content (%)	37.8	21.4	27.8	24.3	24.6
	Absorption (pcf)	7.5	9.1	8.2	7.7	7.5
	Compressive strength (psi)	3290	2270	2920	2320	2000

Note: a) The pcf is pound per cubic yard.

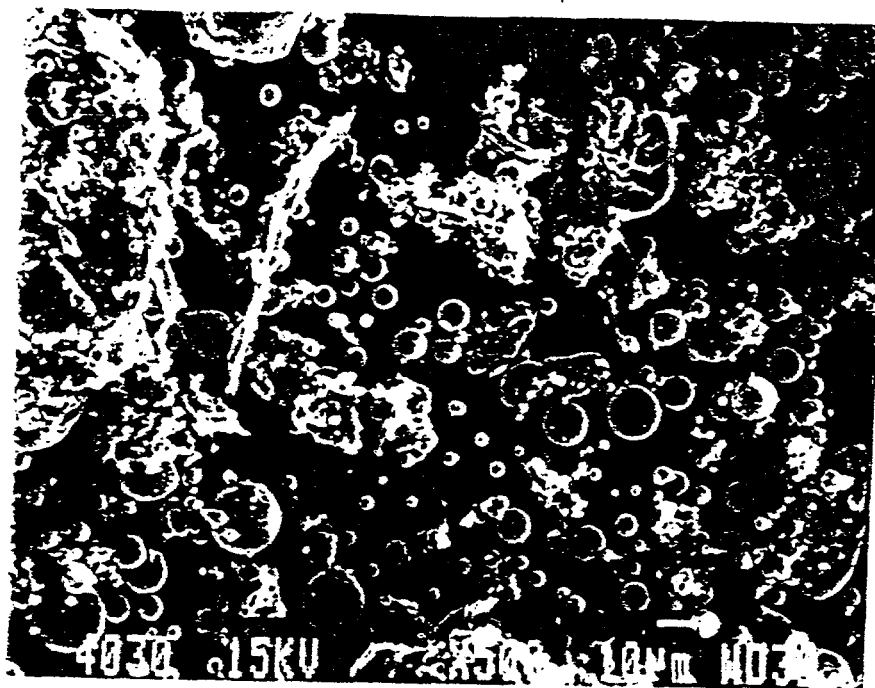


Figure 1 Microstructure of as-received AEP ash

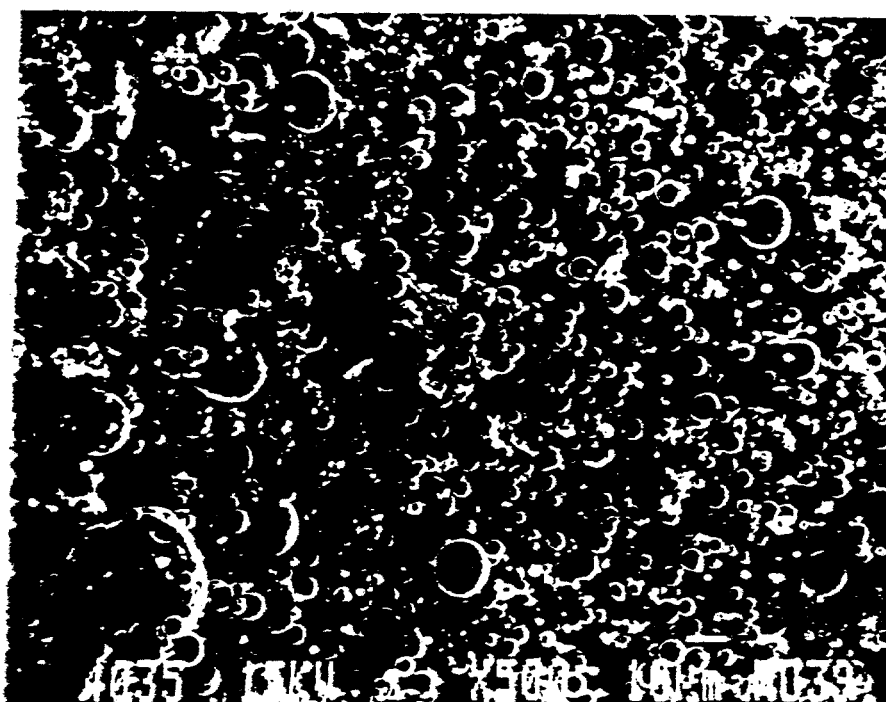


Figure 2 Microstructure of cleaned AEP ash

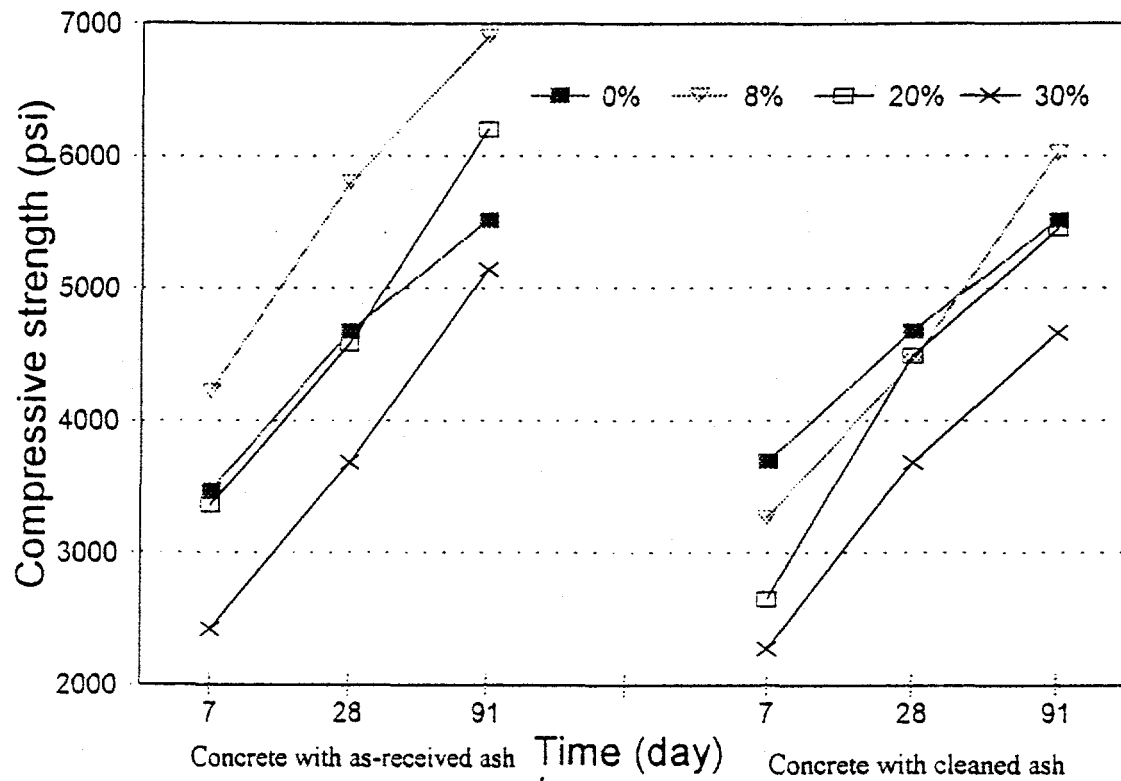


Figure 3 Effects of amount of cement replaced by fly ash and curing period on compressive strength of concrete

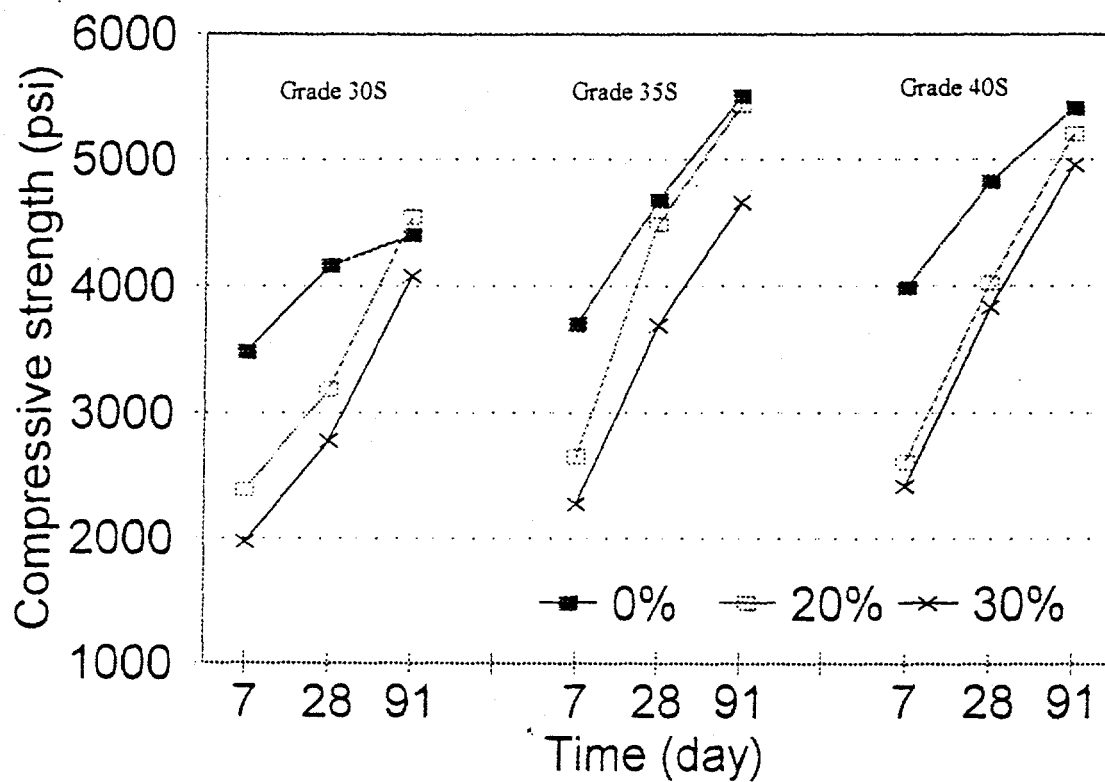


Figure 4 Effects of amount of cement replaced by cleaned fly ash, curing period, and concrete grade on compressive strength of concrete

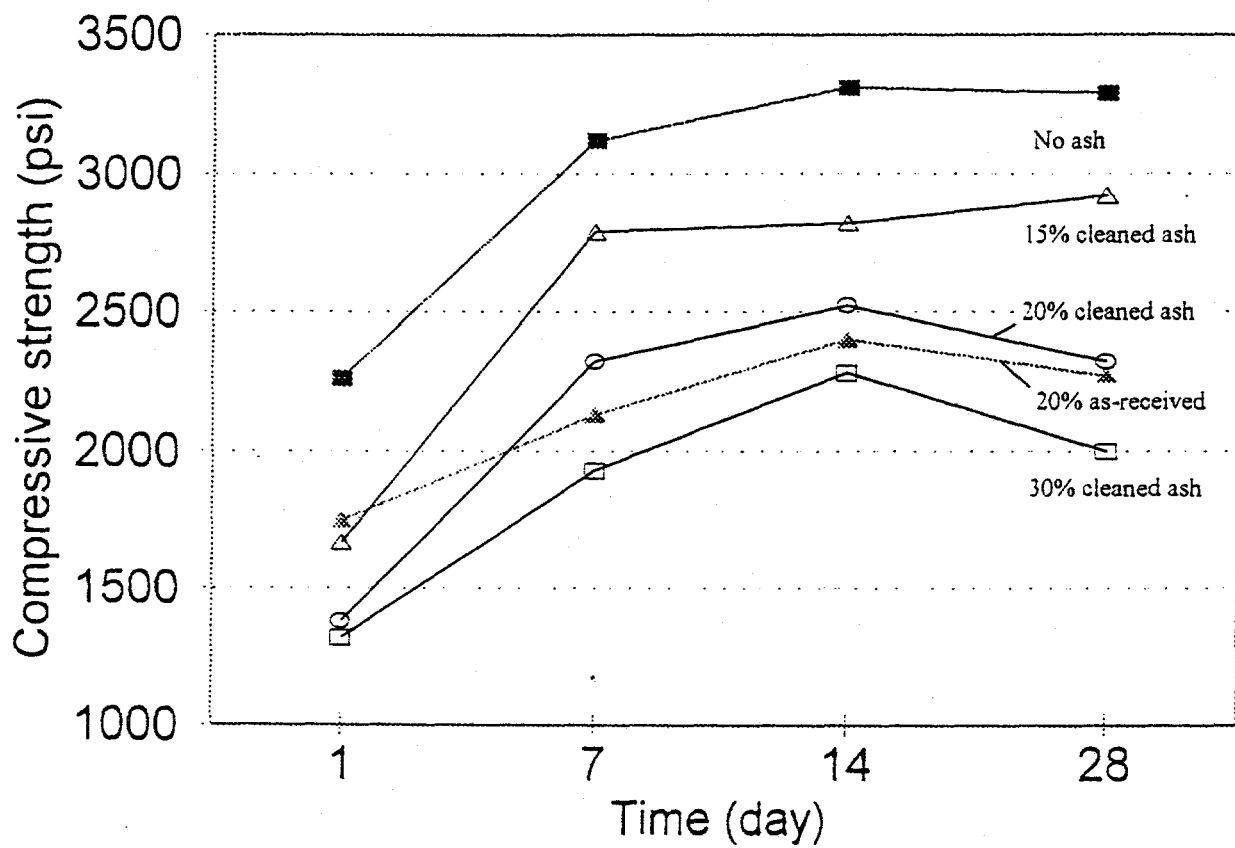


Figure 5 Compressive strength of concrete block

APPENDIX E

Task 4.3 - Plastic Fillers

"Processed Low NO_x Fly Ash as a Filler in Plastics"

**for presentation at
ACAA's 12th International Symposium on Management & Use of Coal Combustion
Byproducts, Orlando, Florida, January 26-30, 1997**

Processed Low NO_x Fly Ash as a Filler in Plastics

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Abstract

Fly ash generated from low NO_x burners at American Electric Power's Glen Lyn facility was beneficiated to remove residual carbon, magnetic particles, and cenospheres. The clean fly ash had a mean particle size of about 30 microns which is coarser than a typical commercial fillers used in plastics. To obtain a finer sized fly ash, air classification was used to separate the clean fly ash into its coarse and fine factions. The resulting fine faction had a mean particle size of 4.13 microns and accounted for 16.7 wt% of the total clean ash. The brightness of the clean ash was also less than that of typical commercial fillers and efforts to improve the brightness proved unsuccessful. The clean ash was then coated with a silane coupling agent and then added to polypropylene, low density polyethylene, and high density polyethylene at various levels. These mixtures were in turn used to make tensile test specimens by injection molding. For comparison, a commercial CaCO₃ filler was also tested under the same conditions. The mechanical properties of these specimens were determined and the results show that the polymers containing fly ash as a filler have equivalent properties to those same polymers when a commercial fillers is used in most cases.

Introduction

The 1990 Clean Air Act Amendments has forced many utilities to retrofit with low NO_x burners to meet the new standards. One side effect of low NO_x burners is that a fly ash with higher carbon content is created, which prohibits its use in cement and concrete products and its potential penetration into a number of other markets.

The Institute of Materials Processing at Michigan Technological University (IMP/MTU) has used its patented beneficiation process to remove the residual carbon, magnetic particles, and cenospheres from low NO_x fly ash at pilot plant scale. As a result the loss on ignition or LOI of the fly ash received from American Electric Power Company (AEP) has been reduced from 23.3% to 1.2%.

A potential application for fly ash, other than as a substitute for cement, is to use the resulting clean ash as a plastic filler. Mineral fillers are widely used in plastic products to improve

performance and reduce the costs. The minerals commonly used for plastic fillers include calcium carbonate, kaolin, aluminum trihydrate, talc and titanium dioxide. Yet calcium carbonate accounts for about 70% of the fillers used.

Fly ash too can be classified as a mineral based on its chemistry and physical natures. The characteristics of fly ash are very close to a number of commercial fillers. Previous studies have indicated that the use of fly ash as a plastic filler has showed promising results^[1-3]. However, the particle size and brightness of fly ash are still less desirable than those of a typical commercial filler. The objective of this research is to further process the clean fly ash by separating the finest fraction and improving its brightness while evaluate its performance as a plastic filler.

Most commercial plastic fillers have a mean diameter of only a few microns. The average particle size of the clean AEP ash is about 30 microns with about 15% having a mean diameter of less than 5 microns. Based on the clean ash size distribution and commercial filler specification, clean ash with a maximum particle size of 5 microns seems an appropriate choice to satisfy the basic plastic filler requirements. Both a hydrocyclone and an air classification system offer a potential means for the separating of fly ash into two fractions using 5 microns as the cut. In this study an air classifier was used for the separation.

The approach adopted in this study to improve brightness was to control the precipitation of TiO_2 , CaCO_3 or ZnO onto the clean ash surface. The evaluation of the fine clean ash coated with a coupling agent as a plastic filler was conducted by comparing it to three polymers, polypropylene, low density polyethylene and high density polyethylene, compounded with a commercial CaCO_3 filler under the same conditions. At the end of the study, a plastic company was invited to try the resulting polymers, compounded with the clean ash, to produce two commercial auto parts.

Experimental

Beneficiation

Ash beneficiation on a pilot plant level was conducted here at the IMP with a feed rate of about 90 kg/hr. The as received fly ash was mixed with water to form a slurry and pumped into a magnetic separator. After the magnetic fraction had been removed, the slurry was fed into a settling tank to capture the cenospheres and provide a uniform feed to a flotation circuit. The cenospheres that floated where in turn recovered by skimming the surface of the water. The under flow material was then pumped into a conditioning tank, where reagents were added into the slurry and then routed to the first bank, or rougher stage, of the flotation phase of the process. A more detailed description on the beneficiation can be found in reference^[4].

Classification

An Acucut air classifier was used for the air classification task. The classification tests initiated with the runs being conducted under different operating parameters to determine the optimum conditions for the cut desired. After each test, the resulting coarse and fine fractions had their

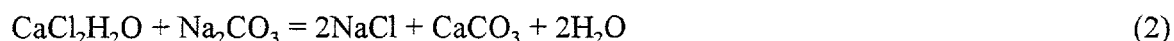
particle size distributions and yields established using a Leeds & Northrup Microtrac. After 12 tests, it was found that Test #10 offered the most favorable results. These parameters were then used to produce more than 3 kg of clean AEP ash with a particle size of less than 5 microns.

Characterization

The most important characteristics for a plastic filler are mean particle size, size distribution, shape, oil absorption, loose density, tap density, brightness, pH, and composition. After air classification had been used to make a cut at 5 microns with the clean AEP ash the resulting fine fraction was characterized according to these properties. The particle size and size distribution was analyzed using a Leeds & Northrup Microtrac analyzer. The particle shape was established using a JEOL JSM 820 scanning electron microscope. The loose density was measured by charging the ash into a 100 ml graduated cylinder weighing the 100 ml ash, and simply dividing the weight by the 100 ml. The tap density was measured by charging ash into a 100 ml graduated cylinder, taping the cylinder 100 times on a Stave 2003 stamp volumeter, measuring the weight and volume, and again simply dividing the weight by the volume. The oil absorption was determined by following the ASTM standard D281. Brightness was determined using a ZEISS photoelectric reflectance photometer with a swing-in brightness standard at brightness of 95.9%. While the pH was measured following the ASTM standard D4972.

Brightness Improvement Test

It was intended to produce TiO_2 , CaCO_3 or ZnO coating on fly ash surfaces by controlling their precipitations. The principle involved is to control the reaction between two materials so that the resulting product will only nucleate and grow on fly ash surface. The TiO_2 , CaCO_3 and ZnO precipitations were produced according to the following reactions:



A slurry with 5% clean ash and two reactant solutions with low concentration but proper ratios based on the above reactions were prepared. The two reactant solutions were charged into 250 ml burets and very slowly fed into a beaker containing the fly ash slurry and being stirred.

Polymers

In order to promote industrial application, Soo Plastics in Sault Ste. Marie, Michigan was been

contacted. This company donated polypropylene, low density polyethylene, and high density polyethylene, which are currently being used by Soo Plastics, to IMP/MTU for this research. These polymers are polypropylene homopolymer T-3922 nat., Escorene LL 6407.67 nat. linear low density polyethylene, and HXM 50100 nat. high density polyethylene. These polymers were produced by Fina Oil & Chemical Company, Exxon Chemical Americas, and Phillips Petroleum, respectively.

Filler Surface Treatment

A Silane coupling agent was coated on the filler surface to improve bonding between the filler surface and the matrix of the polymer. Silane is a series of products formulated for different filler and polymer systems and is one of the most commonly used coupling agent. After consulting with the Dow Corning Corporation, a silane manufacturer, Dow Corning Z-6032 was selected for testing. This silane is suitable for fly ash and compatible with the three polymer systems selected, with properties as outlined in Table 1. Dow Corning donated the Z-6032 for this project. The fine ash was in turn coated with the silane, using the procedure given in Table 2.

Table 1

Typical Properties of Dow Corning Z-6032 Silane

Functionality	vinylbenzyl-amine-methoxy
Percent Solids	40
Solvent	methanol
Specific Gravity at 25°C	0.900
Flash Point, closed cup, °C	13
Viscosity, at 25°C, cSt	2
Suitable diluents	alcohols, water
Shelf life (from date of shipment), months	6

Table 2

Silane Coating Procedure

Step	Activity
1	Silane amount = 0.5 weight percent of ash
2	Silane dilution: add 100 times by weight distilled water
3	Mix the silane solution with ash for 10 minutes
4	Oven dry the slurry
5	Crush the coated ash powder through a 100 mesh screen

Commercial Calcium Carbonate Filler

A commercial CaCO_3 filler commonly used with polymers, Gama-Sperse CS-11, was acquired

from the Georgia Marble Company. This filler has been precoated with 1% stearate by the manufacturer and no additional coupling agents were added to the calcium carbonate in this study. The characteristics of this filler are listed in Table 7.

Polymer and Filler Mixing

Polypropylene, low density polyethylene, and high density polyethylene were compounded with the fine ash fraction as well as the commercial calcium carbonate filler. Each polymer was compounded with ash and then compounded with calcium carbonate at concentrations of 0, 10, 20, 40 and 80 parts per hundred parts of resin (phr). Each of the batches were mixed for 30 minutes in a Brabender Plasti-Corder torque-rheometer at 50 RPM. The mixing temperatures were 250C, 190C and 200C for polypropylene, low density polyethylene, and high density polyethylene respectively.

Injection Molding Test

Injection molding is one of the primary forming processes used by the plastic industry to produce various products. In this research, an Arburg 221-75-350 injection molding machine with a four-cavity standard tensile specimen mold was used for the forming of the test specimens. This machine is capable of providing 35 tons of clamping force and 7.5 tons of injection force. The multi-cavity mold is jacketed with water being used for the heating or cooling of the mold. The water temperature was in turn controlled by a Model TDW-INX conditioner, manufactured by Application Engineering Corporation. If a polymer and filler mixture proved to be injection moldable, ten tensile specimens were produced from each batch for mechanical testing.

Mechanical Testing

The modules of elasticity, elongation, yield and ultimate strengths of the specimens produced by injection molding were determined using an Instron testing system following the ASTM standard D638. If the elongation of a specimen was less than 40%, the elongation was measured by an extensometer automatically. If the elongation of a specimen was greater than 40%, the elongation was measured manually.

Fracture Surface Examinations

Observations were made with the assistance of SEM on the fracture surfaces of the broken tensile specimens to examine the bonding between the polymers and the fillers.

Demonstration of Commercial Manufacturing

Arrangements were made with a local plastics firm that would allow for the injection molding of various commercial products using the compounds produced. These compounds were in-turn granulated down to a size that would flow freely from the feed hopper through the feed chute and into the barrel of a commercial injection molding machine.

The three polymers used in this project were compounded with the fine fraction of the clean AEP ash. The resulting three compounds were used to produce two different automotive parts, a trim clip being used by Chrysler and a component to support an under the hood wiring harness used by General Motors. The trim clip was chosen as a result of the symmetrical cavity layout and because the major surfaces were parallel and perpendicular to the runner. In addition the GM part contained large radii and smooth surfaces that would provide a good indication of the surface quality that could be expected from compounds containing fly ash.

Results and Discussion

Beneficiation

The chemical compositions and LOIs of the AEP fly ash before and after the beneficiation are compared in Table 3. This table shows that the LOI of the AEP fly ash has been reduced from 23.3% to 1.2%, an indication of the effectiveness of the MTU's beneficiation process in removal of residual carbon. As indicated in the table concentrations of the component's other than carbon have increased considerably as a result of the large amount carbon removed using the MTU process. However, it should be noted that Fe_2O_3 has not increased as much, which is due to the removal of magnetic particles during the magnetic separation phase of the process.

Table 3

Chemical compositions of as-received and clean AEP fly ash

Components	As-Received AEP Fly Ash, %	Clean AEP Fly Ash, %
SiO_2	44	58.25
Al_2O_3	22.35	28.57
Fe_2O_3	5.29	5.32
MgO	0.86	1.06
CaO	0.76	0.9
Na_2O	0.32	0.43
K_2O	2.35	2.98
TiO_2	1.11	1.21
P_2O_5	0.03	0.28
MnO	0.01	0.02
Cr_2O_3	0.017	0.015
Ba, ppm	1223	1511

Sr, ppm	978	1129
Zr, ppm	194	278
Y, ppm	63	82
LOI, %	23.3	1.2
Sum, %	100.75	100.67

Classification

Table 4 presents the air classification results of a few tests. As indicated test #10 resulted in the most favorable separation with a 16.7% yield and a mean particle size of 4.13 microns. In turn the operating parameters associated with this test were used to produce more than 3 kg of fine ash. Table 5 shows two particle size distribution analyses of the samples taken from the bottom and top of the 3 kg batch. The two analyses results are very close and show a relatively narrower size distribution of the fine ash. The mean particle sizes of the bottom and top samples are 3.96 and 4.19 microns respectively.

Table 4

Air classification results

Test No.	Coarse Fraction		Fine Fraction	
	Mean Size Microns	Yield %	Mean Size Microns	Yield %
4	28.11	95.4	3.46	4.6
5	35.12	94.6	2.95	5.4
6	33.10	92.2	3.13	7.8
7	39.59	86.1	4.25	13.9
8	36.20	97.9	2.61	2.1
9	29.04	99.3	2.71	0.7
10	38.27	83.3	4.13	16.7
11	37.69	82.3	4.65	17.7
12	37.33	88.9	21.18	11.1

Table 5

Particle size distribution of fine clean AEP ash

Particle Size Microns	Bottom Sample		Top Sample	
	Cumulative, %	Volume, %	Cumulative, %	Volume, %
22	100.0	0.0	100.0	0.0
16	100.0	0.8	100.0	1.6
11	99.2	5.1	98.4	6.1
7.8	94.2	13.8	92.4	15.3
5.5	80.4	21.0	77.1	22.1
3.9	59.4	24.0	55.0	22.3
2.8	35.4	19.9	32.7	18.2
1.9	15.4	8.3	14.5	7.8
1.4	7.1	5.2	6.7	4.9
0.9	1.9	1.9	1.8	1.8

Characterization

The particle shape associated with the fine fraction of the clean AEP ash is shown in Figure 1. They are all spherical except a very few irregular shaped impurities. The particle size distribution has been given in Table 5. The mean particle size, loose and tap densities, brightness, pH, and oil absorption of this ash are presented in Table 6. Table 7 shows the characterization of a commercial calcium carbonate filler and a commercial alumino-silicate filler. Table 8 gives the particle size distribution information of the two fillers. Figure 2 shows the alumino-silicate filler's shape. In comparison with the commercial fillers, the fly ash filler has similar mean particle size, narrower size distribution, a reduced variation in the loose and tap densities, and similar oil absorption to that of alumino-silicate filler. The pH of the fly ash filler also falls between the two commercial fillers. The major differences are the lower brightness and spherical shape of the fly ash filler. While the lower brightness of the ash may slightly reduce the potential spectrum of applications the spherical shape of the ash particle could improve the structural characteristics of polymers compounded with ash resulting in a very broad spectrum of industrial or "under the hood" applications where brightness is not a factor.

Table 6
Characteristics of fine clean AEP ash as a plastic filler

Properties	AEP-C-4M
Mean particle size, microns	4.13
Loose density, g/cc	0.804
Tap density, g/cc	0.874
Brightness	24.2
pH	6.6
Oil absorption	30

Table 7
Characteristics of Commercial Calcium Carbonate and Alumino-Silicate Fillers

Properties	Calcium carbonate filler Gama-Sperse CS-11	Alumino-silicate filler ASP 400P
Mean particle size, microns	3.0	4.8
Loose density, g/cc	0.56	0.38
Tap density, g/cc	n/a	0.72
Brightness	94	79-82
pH	9.5	3.5-5.0
Oil absorption	16	30-35

Table 8

Particle Size Distributions of Calcium Carbonate and Alumino-Silicate Fillers

Particle Size Microns	Gama-Sperse CS-11		ASP 400P	
	Cumulative, %	Volume, %	Cumulative, %	Volume, %
22	100.0	0.0	100.0	6
16	100.0	4.5	94	7
11	95.5	9.5	87	10
7.8	86.0	13.5	77	21
5.5	72.5	15.0	56	14
3.9	57.5	17.5	42	12
2.8	40.0	12.0	30	10
1.9	28.0	6.0	20	6
1.4	22.0	7.5	14	7
0.9	14.5	14.5	7	7

Brightness Improvement Test

It has been established in our studies that TiO_2 and CaCO_3 crystals formed by very slow precipitation are transparent and have tendency not to nucleate on the fly ash surfaces. Figure 3 is an example of the CaCO_3 precipitation coating. The cubic particles are CaCO_3 crystals and the spheres are fly ash. Both the TiO_2 and CaCO_3 coating tests have not been able to improve the brightness of fly ash. While the precipitated $\text{ZnO}/\text{Zn}(\text{OH})_2$, as indicated in the SEM image (Figure 4), surrounds the entire fly ash surfaces with the intent to nucleate on the surface. Yet the brightness of fly ash has not been improved. The precipitation of pure $\text{ZnO}/\text{Zn}(\text{OH})_2$ without fly ash as nuclei was also conducted and resulted in a very white surface. One possible reason for the large brightness difference would possibly be attributed to the contamination from the various fly ash impurities leaching out and affecting the reaction. Another possible reason could be that the coating was too thin.

In an attempt to identify the problem a multilayer coating was tried. The resulting fly ash particles had grown from an initial size of about twenty microns to a few hundred microns with additional coatings, yet the brightness showed no improvement. A comparison test was also made using a steel stirrer and a polymer coated magnetic bar stirring the pure ZnO precipitation. The ZnO precipitations using a magnetic bar as a stirrer were brighter than that using a steel stirrer, which indicated a iron contamination from the steel. A leaching test, adding different amount of HCl in fly ash slurry

resulted a yellowish solutions. ICP analyses of these solutions revealed that many elements are leachable from fly ash when the fly ash is slurred in an acid solution. Table 9 shows the ICP analysis results. The current pH of the coating slurry is about 6. We also found that a longer settling time resulted in a darker appearance. These results indicate that the elements being leached out from fly ash during a coating test caused contamination, resulting in an off-white color.

Table 9
Chemical composition of the solution after fly ash leaching

Leaching Test Results			
Content in Leaching Solution, ppm			
Element	X1FLY	X2FLY	X3FLY
Si	66.39	65.2	66.9
Mg	23.74	28.23	25.44
Mn	0.7236	0.7432	0.7566
Pb	1.206	1.201	1.233
Ba	8.077	8.338	8.841
K	32.79	35.05	37.04
Na	6.458	6.831	7.83
Ni	0.7788	0.7787	0.896
Al	273.9	285.6	288.6
Ca	88.54	95.32	89.07
Fe	84.79	91.86	86.51
Zn	3.875	3.867	2.046
Cu	1.419	1.522	1.45
P	10.3	10.27	10.63

Injection Molding Tests

The addition of a filler to a polymer increases the viscosity of the resulting compound when the polymer is melted by the addition of heat. This increase in viscosity decreases the polymers

moldability. If the addition of filler is over a certain level, the compound may become so viscous that it cannot be injection-molded. In some applications, higher filler loading is required to achieve the targeted properties. In turn it would be desirable to have a fill that would be capable of higher loading for wider applications. In this study, the resulting compounds were injection-molded at the conditions of intentionally lower temperature and lower pressure. If the polymer compounds could not be injected, the injection pressure was gradually increased until the compound could be injected fully into the mold. If the maximum pressure could not inject the compound, the mold temperature was increased gradually without surpassing the upper limit of the suggested injection temperature for the polymer. Table 10, 11 and 12 list the injection molding parameters for the polypropylene, low density polyethylene, and high density polyethylene compounds as well as the various concentrations of fine AEP ash and the commercial calcium carbonate fillers used.

Filler levels, using either AEP ash or calcium carbonate, at or below 80 phr in polypropylene did not result in any difficulties in the injection molding of the compounds. Each were injection-molded under the conditions listed in Table 10.

The addition of fillers in the low density polyethylene decreased the moldability of the compound more significantly. The injection pressure had to be increased to overcome the increase in viscosity as the filler content increased. The low density polyethylene with 40 phr fly ash required 700 psi injection pressure, while the same polymer with 40 phr calcium carbonate filler required 900 psi pressure, as shown in Table 11. When the loading level increased to 80 phr, the low density polyethylene with fly ash was still moldable but the same polymer with calcium carbonate filler was not even though the injection pressure had been increased to the maximum 2200 psi.

The high density polyethylene proved more difficult to inject because of its higher viscosity. The injection pressure had to be greater than 1200 psi in order to fully fill the mold cavity even for the pure polymer. The addition of fly ash filler in the levels below or equal 40 phr did not cause any injection problems, but the addition of calcium carbonate filler in the amount of 40 phr introduced a significant increase in viscosity. The injection pressure had to be adjusted to the maximum of 2200 psi, the mold temperature was raised from 100F to 140F, and the injection temperatures had to be increased to the highest suggested temperatures for this polymer, but this compound still could not be injected into the cavity fully.

These injection molding tests indicated that polypropylene, low and high density polyethylenes compounded with fine AEP ash have similar or better moldability than their counterparts when compounded with a commercial calcium carbonate filler.

Table 10

Injection Molding Test of Polypropylene with Fillers

Fillers	Filler Content phr	Zone I Temp. °C	Zone II Temp. °C	Zone III Temp. °C	Zone IV Temp. °C	Injection Velocity Dial*	Injection Pressure psi	Holding Pressure psi	Mold Temp. °F
None	0	210	220	210	200	5.0	400	100	100
Fly Ash	10	210	220	210	200	5.0	400	100	100
CaCO ₃	10	210	220	210	200	5.0	400	100	100
Fly Ash	20	210	220	210	200	5.0	400	100	100
CaCO ₃	20	210	220	210	200	5.0	400	100	100
Fly Ash	40	210	220	210	200	5.0	400	100	100
CaCO ₃	40	210	220	210	200	5.0	400	100	100
Fly Ash	80	210	220	210	200	5.0	400	100	100
CaCO ₃	80	210	220	210	200	5.0	400	100	100

* Dial 5.0 is the maximum injection velocity of the machine.

Table 11

Injection molding test of low density polyethylene with fillers

Fillers	Filler Content phr	Zone I Temp. °C	Zone II Temp. °C	Zone III Temp. °C	Zone IV Temp. °C	Injection Velocity Dial*	Injection Pressure psi	Holding Pressure psi	Mold Temp. °F
None	0	210	220	210	200	5.0	500	100	100
Fly Ash	10	210	220	210	200	5.0	500	100	100
CaCO ₃	10	210	220	210	200	5.0	500	100	100
Fly Ash	20	220	230	220	210	5.0	700	100	100
CaCO ₃	20	220	230	220	210	5.0	700	100	100
Fly Ash	40	220	230	220	210	5.0	700	100	100
CaCO ₃	40	220	230	220	210	5.0	900	100	100
Fly Ash	80	220	230	220	210	5.0	900	150	100
CaCO ₃ *	80	240	250	240	230	5.0	2200	150	120

* This material can't be injected even at the maximum pressure 2200 psi.

Table 12

Injection molding test of high density polyethylene with fillers

Fillers	Filler Content phr	Zone I Temp. °C	Zone II Temp. °C	Zone III Temp. °C	Zone IV Temp. °C	Injection Velocity Dial*	Injection Pressure psi	Holding Pressure psi	Mold Temp. °F
None	0	260	260	250	250	5.0	1200	100	100
Fly Ash	10	260	260	250	250	5.0	1200	100	100
CaCO ₃	10	260	260	250	250	5.0	1200	100	100
Fly Ash	20	260	260	250	250	5.0	1200	100	100
CaCO ₃	20	260	260	250	250	5.0	1200	100	100
Fly Ash	40	260	260	250	250	5.0	1200	100	100
CaCO ₃ *	40	290	290	270	270	5.0	2200	100	140

* This material can't be injected even at the maximum pressure 2200 psi.

Mechanical Properties

The ultimate tensile strength, yield strength, elongation and Young's modules are the most important mechanical properties for polymer materials. Filler content, filler particle size, size distribution, shape, mixing quality, and bonding between filler and polymer matrix all affect the mechanical properties. As a rule, higher filler content leads to higher yield strength and an increase in the Young's modules while a lower elongation would be expected because the filler particles restrict deformation of the polymers. The fillers also affect the ultimate tensile strength (UTS) in two ways. First, the filler particles cause stress concentration and initiate cracks, lowering UTS. Second, if the particles have the proper shape and a strong bonding between the particles and the polymer matrix, the particles may serve to reinforce polymer, resulting in higher UTS. With regard to size the larger particles usually reduce the UTS and elongation.

Table 13 represents the mechanical properties of polypropylene with fly ash and calcium carbonate fillers. This table indicates that the yield strength and Young's modules increase and UTS and elongation decrease as the filler content increases, except when calcium carbonate content is over 40 phr. At this level the calcium carbonate filler begins to decrease the yield strength as well as the Young's modules. With lower calcium carbonate contents of 10 and 20 phr, the polypropylene compound shows higher UTS than those of the polymers with fly ash filler. When the calcium carbonate content exceeds 40 phr, the UTS of the compound is lower than that of the compounds with ash as the filler. The yield strength and Young's modules of the polypropylene with an ash filler are higher than those of the polypropylene with calcium carbonate filler, but the elongation is lower than that of the counterpart. In general, ash filler can

replace calcium carbonate filler to reach the equivalent mechanical properties when the filler content is less than or equal to 20 phr.

Table 14 shows the results of the mechanical tests for the low density polyethylene with ash and calcium carbonate fillers. The low density polyethylene with ash filler have better mechanical properties than those of the same polymer with calcium carbonate filler. This superiority is more obvious at the higher loading level of 40 phr.

Table 15 gives the mechanical properties for the high density polyethylene with ash and calcium carbonate fillers. The noticeable phenomenon is that the UTS increases when filler content reaches 40 phr for the polymer with ash filler. This indicates that the ash filler may reinforce the polymer matrix. Over all, the high density polyethylene with an ash filler has better strengths and Young's modules than those of the polymer with calcium carbonate filler, but the elongation is not as good as its counterpart.

Table 13

Mechanical properties of polypropylene with fillers

Fillers	Filler Content phr	Ultimate Tensile Strength, psi	Yield Strength psi	Elongation %	Young's Modules, ksi
None	0	6666	1728	650	185
Fly Ash	10	4724	2199	630	189
CaCO ₃	10	5024	1880	650	164
Fly Ash	20	4378	2340	467	211
CaCO ₃	20	4928	2114	600	178
Fly Ash	40	4267	2416	32	237
CaCO ₃	40	3850	1738	367	125
Fly Ash	80	3953	2474	1.3	314
CaCO ₃	80	2900	1480	41.7	217

Table 14

Mechanical properties of low density polyethylene with fillers

Fillers	Filler Content phr	Ultimate Tensile Strength, psi	Yield Strength psi	Elongation %	Young's Modules, ksi
None	0	3336	485	467	27.5
Fly Ash	10	3463	557	467	36.0
CaCO ₃	10	3255	545	467	33.4
Fly Ash	20	2635	560	462	39.4
CaCO ₃	20	2563	573	483	33.6
Fly Ash	40	2449	738	450	47.3
CaCO ₃	40	1905	574	442	33.6
Fly Ash	80	2377	888	46.6	90.5
CaCO ₃	80	-	-	-	-

Table 15

Mechanical properties of high density polyethylene with fillers

Fillers	Filler Content phr	Ultimate Tensile Strength, psi	Yield Strength psi	Elongation %	Young's Modules, ksi
None	0	5040	1016	60	79.4
Fly Ash	10	4843	1192	45	73.2
CaCO ₃	10	3807	940	83	45.2
Fly Ash	20	4823	1160	50	81.6
CaCO ₃	20	3698	1089	84	56.6
Fly Ash	40	5219	1279	28	96.4
CaCO ₃	40	-	-	-	-

Fracture Surface Examinations

SEM images indicate that in general, fillers have been homogeneously mixed with the polymers. Figure 5 to 10 show the fracture surfaces of the polypropylene, low density polyethylene and high density polyethylene with 40 phr of ash filler and calcium carbonate filler respectively. Good bonding between the ash filler and the three polymers can be seen in Figure 5, 7, and 9. Figure 6, 8 and 10 give examples of calcium carbonate filler and polymer bonding. It appears that fly ash, along with the silane coupling agent, has better bonding with the three polymers than the calcium carbonate does.

Demonstration of Commercial Manufacturing

A VanDorn, Model #75-RS-4F, injection machine was used to process the ash filled compounds. With VanDorn being a large and well established producer of injection molding machines, the use of this machine would provide a very good representation of the typical injection molding machine used today. Injection of the trim clip was carried out first because it was a much smaller component and in-turn would not be as difficult as to clean up should the experimental materials prove difficult to inject. Yet all went smoothly, material flowed well, cavities were filled uniformly, lines were well defined and parting of the product was realized without the addition of a mold release. The operators, as well as the owner of the business, went on to say that they could not distinguish between the operation of the machine using the experimental compounds and the commercial materials typically used to produce the trim clips. Figure 11 shows the parts produced from one of the polymers with ash filler. The injection of the GM wiring harness support proceeded just as smoothly. Though the shape was of a nature that considerably more resistance would be encountered, the material readily filled the cavities. Adjustments were made to the injection pressure, holding pressure and back pressure yet the new settings were typical of what would be expected given the nature of the die and not a result of the variation in the compound being injected. Figure 12 presents the GM wiring harness supports produced from one of the ash filled polymers.

With the mechanical testing of the tests specimens, produced in the lab, serving to establish the physical properties of the compounds, the primary concern with regard to quality of the products produced was the resulting surface finish. Those materials containing 10 phr displayed very smooth somewhat glossy surfaces. Injection of those compounds containing 20 phr produced parts that had a somewhat opaque finish, yet it was still a very smooth surface. The parts coming out of the mold as the compounds containing 40 phr were feed to the barrel displayed an uneven surface that was dull in nature and revealed flow patterns in many cases. An operator was quick to point out that this was not at all uncommon with compounds containing a considerable amount of filler. He even produced parts that they regularly manufacture for comparison which, from the surface, displayed the same characteristics with regard to the surface quality.

Overall the injection of the ash filled compounds went very smoothly. There were no major problems encountered and the resulting products indicated that a quality finish could be expected when using these materials in the injection molding of commercial products. Which polymers would be best suited for compounding with ash would still need additional study, yet as indicated by this preliminary study, their use as a filler in both high and low density polyethylene as well as polypropylene would certainly be expected to yield considerable benefit.

Conclusions

AEP as-received low NO_x ash can be processed to produce fine clean powders with the characters suitable for plastic filler application. The particle size distribution is narrower than that of two comparable commercial fillers. However, the brightness is about 24, much lower than that of commercial calcium carbonate filler and alumino-silicate filler, which limits its uses to darker color applications. The unique spherical shape can be an advantage over most existing commercial fillers.

The polypropylene, low density and high density polyethylene compounds with fine clean ash filler have equivalent or better moldability for producing articles in comparison with the commercial calcium carbonate filler, Gama-Sperse CS-11.

In general, the polypropylene and high density polyethylene with fine clean ash filler show equivalent or better strengths and Young's modules, but the elongation is not as good as those of the same polymers with the commercial calcium carbonate filler, Gama-Sperse CS-11. The low density polyethylene with the fine clean ash filler shows superiority over the same polymer with calcium carbonate filler in all measured mechanical properties at various loading levels.

The ash filler coated with Dow Corning Z-6032 silane appear to offer very good bonding with the polypropylene as well as the low density and high density polyethylene matrixes.

The polymers with ash filler can be used to produce commercial automotive parts with no difference in injection moldability, dimension accuracy and surface quality in comparison with the commercially filled polymer compounds.

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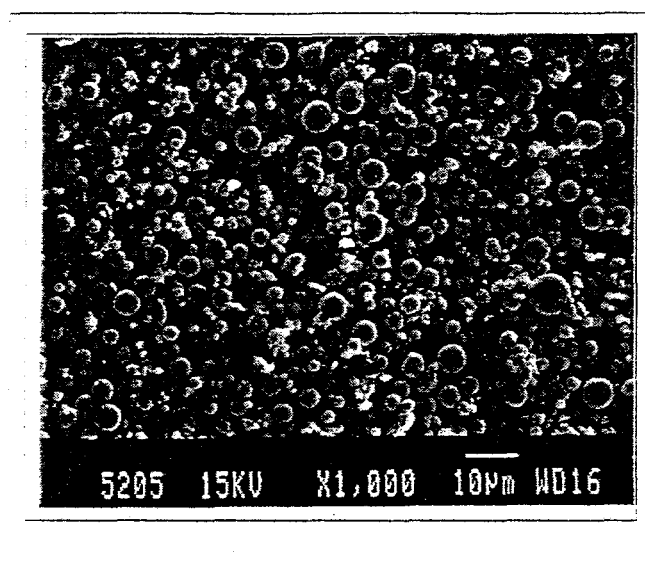


Figure 1. Particle shape of fine clean AEP ash

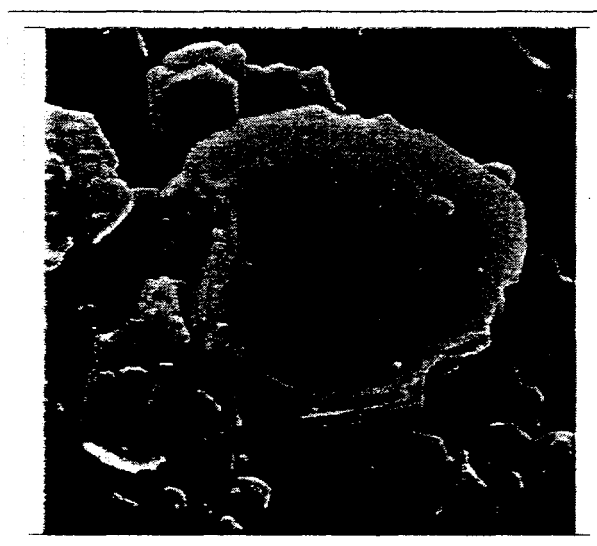


Figure 2. Particle shape of commercial aluminosilicate filler

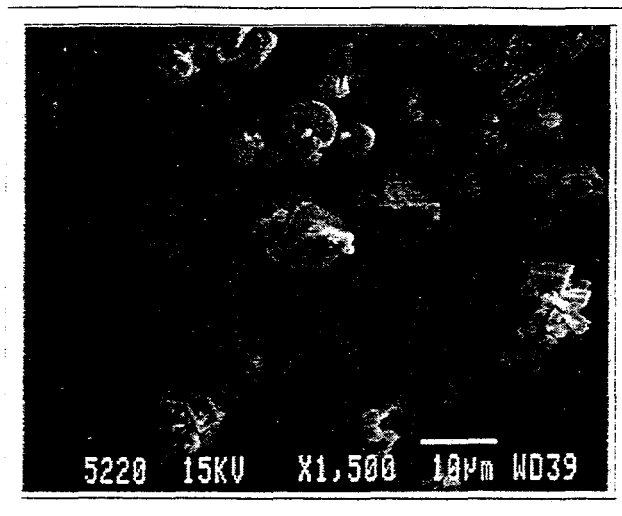


Figure 3. CaCO_3 precipitation on fly ash surfaces

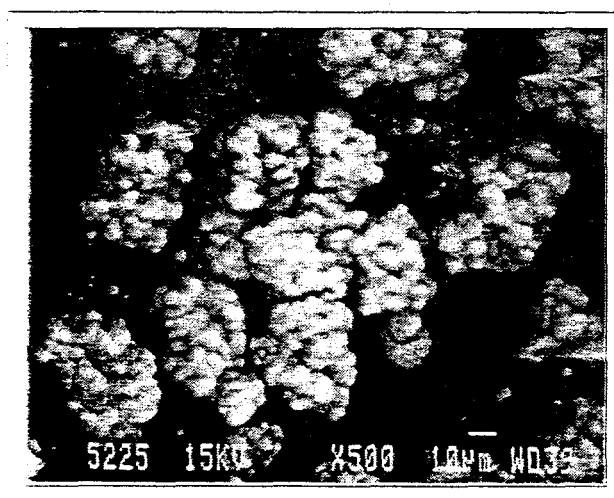


Figure 4. $\text{ZnO}/\text{Zn}(\text{OH})_2$ precipitation on fly ash surfaces

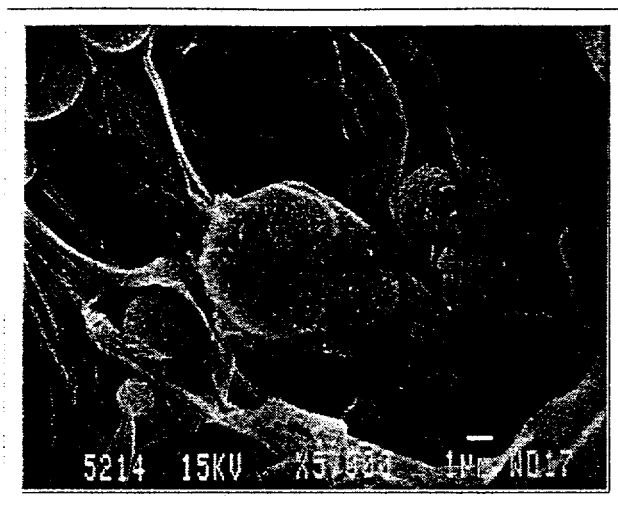


Figure 5. Fracture surface of polypropylene with 40 phr fine clean AEP ash

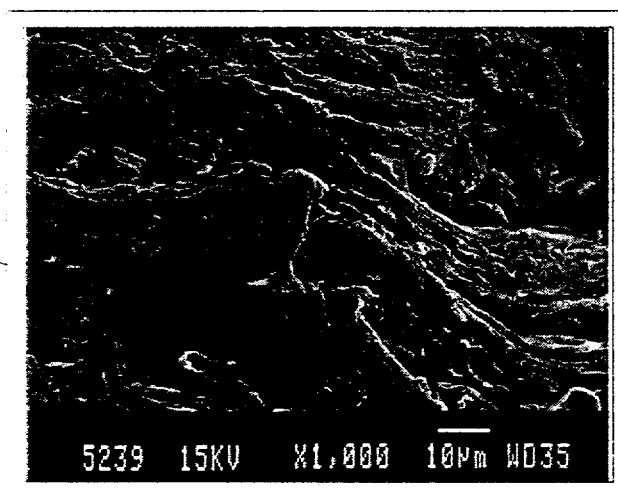


Figure 6. Fracture surface of polypropylene with 40 phr CaCO₃ filler

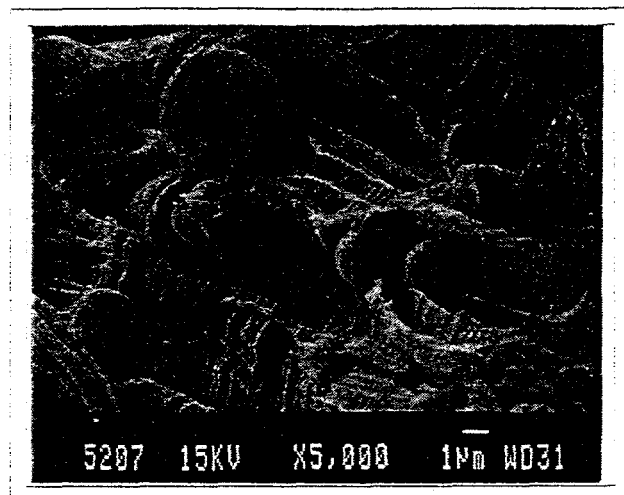


Figure 7. Fracture surface of low density polyethylene with 40 phr fine clean AEP ash

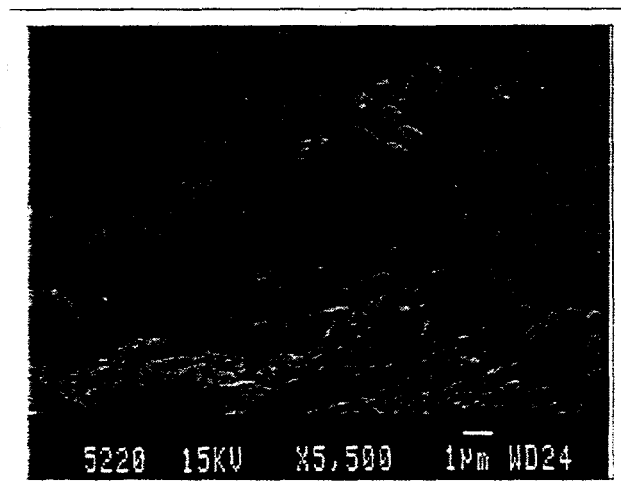


Figure 8. Fracture surface of low density polyethylene with 40 phr CaCO₃ filler

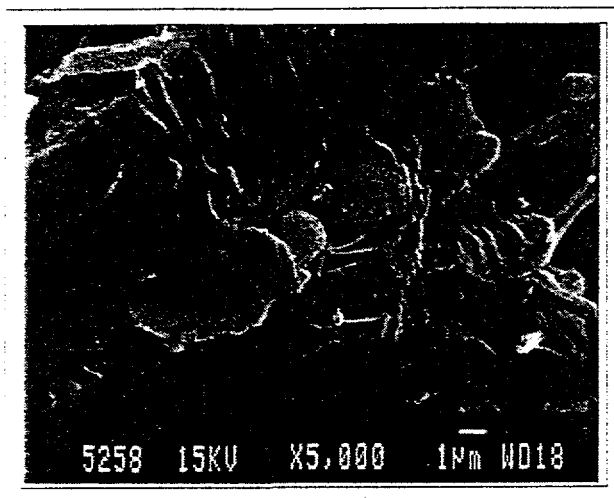


Figure 9. Fracture surface of high density polyethylene with 40 phr fine clean AEP ash

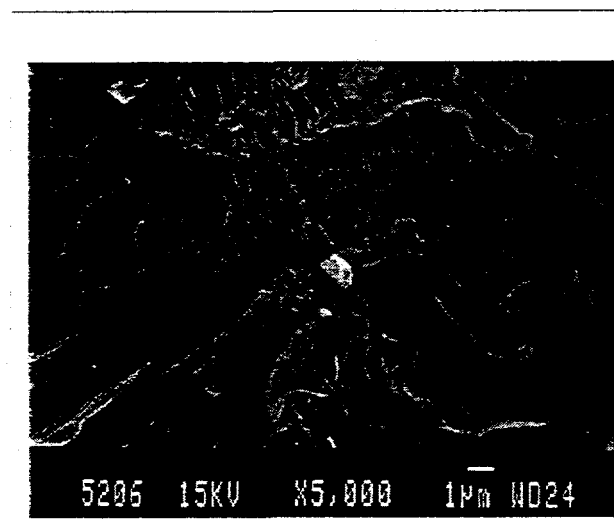


Figure 10. Fracture surface of high density polyethylene with 40 phr CaCO_3 filler

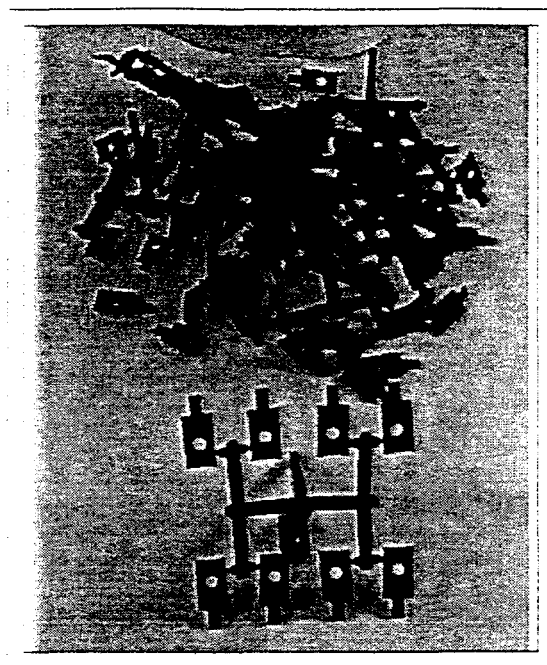


Figure 11. Trim clips produced from one of the ash filled polymers

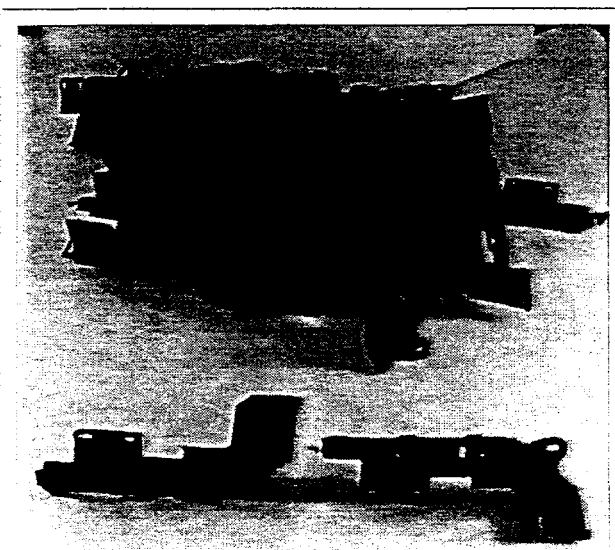


Figure 12. GM wiring harness support produced from one of the ash filled polymers